VOL. XVII. [FEBRUARY, 1895.] NO. 2.

AMERICAN CHEMICAL JOURNAL.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.[1]

BY WOLCOTT GIBBS, M. D., *Rumford Professor Emeritus in Harvard University.*

[*Continued from p.* 417, *Vol.* 7.]

PLATINO-TUNGSTATES.

In a notice of these and corresponding compounds of molybdenum published some years since,[2] and intended to be only preliminary, I pointed out the analogy between them and the silico-tungstates of Marignac. The notice in question requires correction in several particulars, and I shall here give the results of a more complete investigation, conducted with better facilities for work and with a much wider acquaintance with the whole class of complex acids.

Platinic hydrate, like silicic hydrate, dissolves when boiled with solutions of alkaline tungstates belonging to the meta-tungstic series. Platino-tungstates are formed under these circumstances, but various conditions require to be considered. In general, I have been accustomed to prepare the hydrate $Pt(OH)_4$ by Frémy's method, that is, by boiling a solution of platinic chloride with a large excess of sodic hydrate for some

[1] Presented at a meeting of the American Academy of Arts and Science, held August 1, 1894.

[2] Ber. d. chem. Ges., 10, 1384, 1877.

time and then adding acetic acid in small excess, when the platinic hydrate separates as a pale buff-yellow slimy compound to be washed by repeated decantation with cold water. When the last portions of saline matter have been removed the wash-water becomes turbid and settles only after very long standing. The hydrate obtained in this way sometimes dissolves very readily in hot solutions of alkaline tungstates, sometimes only after long boiling, and sometimes is almost insoluble. The process is therefore an uncertain one at best. The platino-tungstates formed have a yellow or orange-yellow color, and, in many cases, crystallize well. By the process which I have given, it is usually difficult to obtain perfectly saturated compounds unless a rather large excess of platinic hydrate is employed. When this is the case a greater or less quantity of a deep orange-red solution is sometimes formed, which, on standing, deposits a dark tarry mass in case the sodic tungstate is employed. In place of sodic hydrate I have also used baric hydrate in preparing a soluble form of the platinum compound, but in this case also the platinic hydrate, according to varying conditions, varied very much in solubility.

When platinic hydrate is boiled with a solution of 10:4 sodic tungstate, the latter being in large excess, yellow solutions are sometimes formed, which, on evaporation and standing, yield large crystalline masses with a fine yellow color and strong luster. These crystals consist essentially of the 10:4 sodic salt, $10WO_3.4Na_2O + 23aq.$, but they contain a greater or less proportion of a platinic compound which—water of crystallization apart—has probably the formula

$$10WO_3.PtO_2.4Na_2O,$$

and which appears to be isomorphous with the tungstate. A compound of this kind gave on analysis figures which corresponded very closely with the formula

$$10WO_3.PtO_2.4Na_2O + 2\{10WO_3.4Na_2O\} + 72aq.$$

We may have here a combination of two isomorphous salts, having, respectively, the formulas, $10WO_3.PtO_2.4Na_2O + 26aq.$, and $10WO_3.4Na_2O + 23aq.$ The analyses of two different preparations of the salts correspond very closely.

The difficulty of obtaining definite compounds by direct

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solution of platinic hydrate led me to another method, which may be used with much advantage. Pure crystallized sodic tungstate is to be dissolved in water, a rather large excess of sodic hydrate added, and a neutral, or nearly neutral solution of platinic chloride added to the boiling solution in small portions at a time. Platinic hydrate is formed and instantly dissolved. The chloride is to be added until a distinct excess of $Pt(OH)_4$ is present. Acetic acid is then to be added in small excess. Alcohol then often throws down a dark tarry mass which contains one or more saturated platino tungstates. When the proportion of platinic chloride necessary, happens to be exact, a beautiful orange-colored clear solution is formed, which, on cooling or evaporation, deposits an abundance of beautiful yellow needles, or prisms, easily purified by recrystallization. By this process a definite salt may be prepared in a very short time and in large quantity. Different salts are, however, formed under different conditions, and further investigations must show whether it is possible, by using definite quantities of platinic chloride and of sodic tungstate, to obtain uniform results as regards the constitution of the salt formed. It is indispensable to employ pure platinic chloride or chlorplatinates. Even traces of iridium give a greenish tint to the platino-tungstates formed, a fact which misled me in my earlier experiments. Contrary to my preliminary statement, I now find, on more prolonged study, no isomeric platino-tungstates.

10:1:6 *Sodic Platino-tungstate.*—12:5 sodic tungstate very readily dissolves platinic hydrate in its soluble form, and gives a fine deep orange-colored solution, which, on standing, yields a mass of ill-defined dull orange crystals. These may be redissolved, recrystallized, and dried on woolen paper. Of these crystals:

1.1460 grams gave 0.8430 gram $Pt + WO_4 = 73.56$ per cent.
1.1806 grams gave 0.0686 gram $Pt + WO_4 = 73.57$ "
1.1806 grams gave 0.0706 gram $Pt = 5.98$ "
1.1460 grams gave 0.8695 gram $Pt = 6.06$ "
1.8770 grams gave 0.7774 gram $WO_4 = 67.83$ "
0.8770 gram lost on ignition 0.1397 gram $O + H_2O = 15.93$ per cent.

The analyses lead to the formula

$$10WO_3.PtO_2.6Na_2O + 28aq.,$$

which requires:

		Calculated.		Mean.		Found.		
$10\,WO_3$	2320	67.79	74.40	67.65	74.65	67.56	67.83	67.57
PtO_2	226.5	6.61		7.00		6.96	7.05	
$6\,Na_2O$	372	10.87	25.60			10.51		25.45
$28\,H_2O$	504	14.73				14.94		
	3422.5	100.00						

The soda being estimated by difference. It is remarkable that this salt contains 6 molecules of base instead of 4, all known silico-tungstates being tetrabasic. The solution of this salt, when shaken with a solution of potassic bromide, gives an amorphous pasty mass with a deep orange-red color. In the analysis of this class of compounds it is best to determine the platinum by ignition with sodic carbonate. On treatment of the fused mass with water, the platinum remains as metal, and the tungsten may then be determined in the filtrate in the usual manner. Nearly all the analyses were made in this way, sodic oxide being determined by difference. In some cases, however, tungstic and platinic oxides were precipitated together by mercurous nitrate and mercuric oxide.

20 : 1 : 9 *Sodic Platino-tungstate.*—In one experiment in which I boiled a portion of pure sodic tungstate with a considerable excess of sodic hydrate, and added to the boiling solution chlorplatinic acid ($PtCl_6H_2$) in small portions at a time, a fine yellow solution was formed, after addition of an excess of acetic acid, which soon deposited a mass of topaz-yellow crystals. This could be redissolved and recrystallized without decomposition. The mother-liquor appeared to contain one or two other salts. Of this salt:

(1) 1.4847 grams lost on ignition 0.2453 gram $O + H_2O =$ 16.52 per cent.

(4) 1.4154 grams lost on ignition 0.2349 gram $O + H_2O =$ 16.61 per cent.

(2) 1.4847 grams gave 0.0466 gram Pt = 3.73 per cent. PtO_2.

(3) 1.0976 grams gave 0.0345 gram Pt = 3.65 per cent. PtO_2.

(5) { 1.4154 grams gave 1.0467 grams Pt = 3.83 per cent.
1.4154 grams gave 1.0129 grams WO_3 = 71.57 per cent.

(6) 1.4847 grams gave 1.0619 grams WO_3 = 71.50 per cent.

The analyses lead to the formula

$$20WO_3.PtO_2.9Na_2O + 58aq.,$$

which requires:

		Calculated.	Mean.	Found.		
$20WO_3$	4640	71.73	71.53	71.57	71.50	
PtO_2	226.5	3.50	3.74	3.73	3.65	3.83
$9Na_2O$	558	8.63	8.68		8.67	
$58H_2O$	1044	16.14	16.05	16.00	16.09	
	6468.5	100.00				

The solution of this salt has a strongly acid reaction with litmus. It gives with ammonic chloride beautiful colorless scaly crystals, slightly soluble in cold, but soluble in boiling water, exactly resembling in appearance the sodio-ammonic tungstate, $12WO_3.Na_2O.4(NH_4)_2O$, and containing no platinum. This reaction seems to support the view that the compound is a double salt, and we may, perhaps, assume that it is represented by the formula

$$10WO_3.4Na_2O + 10WO_3.PtO_2.5Na_2O + 58aq.$$

The principal reactions of this salt are as follows:

With $AgNO_3$, a white fine grained crystalline precipitate settling slowly.

With $TlNO_3$, a similar precipitate in rather coarser grains.

With SO_4Cu, a very pale blue, or bluish-white fine-grained precipitate.

With $HgNO_3$, a bright yellow amorphous precipitate.

With $Co(NH_3)_6Cl_3$, a pale buff precipitate quickly becoming crystalline in leaves.

A quantity of this platino-tungstate was precipitated by a solution of mercurous nitrate. The fine yellow mercurous salt was well washed and then decomposed by dilute chlorhydric acid, the platino-tungstate being in very small excess.

The clear yellow filtrate on spontaneous evaporation deposited a pale yellow substance which may prove to be the corresponding acid.

30:2:15 *Sodic Platino-tungstate.*—This salt was obtained under the same conditions as the last, and formed granular efflorescent dull yellowish crystals readily soluble in water. Of this salt:

1.3231 grams gave 0.9787 gram $WO_3 + Pt = 73.97$ per cent.
1.3231 grams gave 0.0510 gram Platinum $= 4.49$ per cent. PtO_2.
1.0144 grams gave 0.0410 gram Platinum $= 4.70$ per cent. PtO_2.
1.5776 grams lost on ignition with WO_4Na_2 0.2657 gram $O + H_2O = 16.71$ per cent.
1.5776 grams gave 1.1059 grams $WO_3 = 70.06$ per cent.
1.3231 grams gave 0.9271 gram $WO_3 = 70.03$ per cent.

The analyses lead to the formula

$$30WO_3.2PtO_2.15Na_2O + 89aq.,$$

which requires:

		Calculated.	Found.	
30 WO_3	6960	69.98	70.03	70.06
2 PtO_2	453	4.56	4.49	4.70
15 Na_2O	930	9.35	9.24	
89 H_2O	1602	16.11	16.18	
	9945			

A solution of this salt also gives white scaly crystals with potassic and ammonic salts. It gives a white flocky precipitate with baric chloride, and a pale yellow flocky crystalline precipitate with mercurous nitrate. The compound is probably, like the last described, a double salt and may have the formula

$$10WO_3.3Na_2O.H_2O + 2\{10WO_3.PtO_2.6Na_2O\} + 88aq.$$

The solution of the salt is acid to litmus. Analysis by Dr. Morris Loeb.

30:1:12 *Sodic Platino-tungstate.*—I obtained this salt by boiling platinic hydrate with 10:4 sodic tungstate for some time in a platinum vessel. It formed very large masses of

honey-yellow heavy crystals, very easily soluble in water. Of this salt:

1.1441 grams lost on gentle heating 0.1583 gram H_2O=13.84 per cent.

0.9383 gram lost on gentle heating 0.1313 gram H_2O=13.99 per cent.

1.8069 grams gave 1.4033 grams WO_3+Pt=77.66 per cent.

0.8809 gram gave 0.6847 gram WO_3+Pt=77.72 per cent.

[1] —— gram gave —— gram Platinum =2.46 per cent. PtO_2.

The analyses agree with the formula

$$30WO_3.PtO_2.12Na_2O+72aq.,$$

which requires:

		Calculated.	Found.	
$30WO_3$	6960.0	75.44	75.53	75.43
PtO_2	226.5	2.45	2.46	
$12Na_2O$	744.0	8.06	8.15	
$72H_2O$	1296.0	14.05	13.84	13.99
	9226.5	100.00		

In the analyses the water was determined by heating in an air-bath, and not by ignition. No correction for oxygen of PtO_2 is therefore applied. The solution of the salt gives the characteristic white scaly crystals with NH_4Cl and KCl, and as in the last two cases we may safely assume that the compound is a double salt. The most probable formula considering the mode of formation is

$$10WO_3.PtO_2.4Na_2O+2\{10WO_3.4Na_2O\}+72aq.$$

From the above it appears that, strictly speaking, none of the compounds described correspond to the silico-tungstates of Marignac, all of which appear to contain four molecules of basic oxide. Such platinum compounds may, however, exist in combination, as seems to be shown in the salts last described.

The other metals of the platinum group will probably be found to form similar compounds. Want of material has prevented a careful study of the subject, but a number of qualitative tests made with small quantities of salts of iridium, ruthenium, palladium, and osmium appeared to show clearly

[1] The data of this analysis were accidentally lost.

that these metals also form compounds with tungstic and molybdic oxides analogous to those of platinum.

8 : 2 : 3 *Platino-molybdate of Ammonium.*—When freshly prepared sodic platinate, $Na_2O.3PtO_2$, is boiled with a solution of 14 : 6 ammonic molybdate, it readily dissolves to an orange-yellow liquid, which, after a time, deposits beautiful lemon-yellow crystals, which may be easily purified by recrystallization. The salt dissolves rather easily in cold, and very readily in hot water. The solution gives with argentic nitrate a pale yellow flocky precipitate which becomes crystalline on standing. With mercurous, mercuric, and thallous nitrates it gives pale yellow flocky precipitates not distinctly crystalline and settling quickly. With nitrate of croceo-cobalt the solution gives a beautiful bright yellow crystalline salt. The formula of the ammonium salt is

$$8MoO_3.2PtO_2.3(NH_4)_2O + 12aq.$$

as the following analyses show:

1.7831 grams gave 0.3554 gram Pt = 19.94 per cent. = 23.21 per cent. PtO_2.

0.5425 gram gave 0.1075 gram Pt = 19.82 per cent. = 23.09 per cent. PtO_2.

0.4354 gram gave 0.0868 gram Pt = 19.92 per cent. = 23.15 per cent. PtO_2.

1.0407 grams gave 0.0535 gram NH_3 = 5.14 per cent.

0.5149 gram gave 0.0405 gram NH_3 = 5.14 per cent.

0.5878 gram gave 0.0459 gram NH_3 = 5.14 per cent.

1.2015 grams lost on ignition with WO_4Na_2 0.2663 gram = 22.17 per cent. $H_2O + NH_3 + O$.

0.8368 gram lost on ignition with WO_4 0.1876 gram = 22.42 per cent. $H_2O + NH_3 + O$.

		Calculated.	Mean.	Found.		
8 MoO_3	1152	58.27	57.83			
2 PtO_2	453	22.91	23.15	23.21	23.09	23.15
6 NH_3	102	5.16	5.14	5.14	5.14	5.14
15 H_2O	270	13.66	13.88	13.76	14.01	
	1977	100.00				

Other salts of this series may be prepared from the ammo-

nium salt by precipitating its solution with mercurous nitrate and decomposing the well-washed mercurous salt by solutions of the chlorides of other metals.

4 : 2 : 2 *Platino-molybdate of Ammonium.*—The solution from which the yellow ammonium salt, first described, separated by crystallization gave, on evaporation, a dark-colored liquid over a heavy oily deep brown-red substance. This last was washed with a little ice-cold water and gradually dried to a transparent dark brown-red mass which broke up into clean sharp brilliant fragments. Of this salt:

0.4502 gram lost on careful heating 0.1297 gram = 28.81 per cent. $H_2O + NH_3 + O$.

0.4502 gram gave 0.1226 gram Platinum = 31.63 per cent. PtO_2.

0.5398 gram gave 0.0402 gram $(NH_4)_2O$ = 4.91 per cent. NH_3.

0.4917 gram gave 0.0369 gram $(NH_4)_2O$ = 4.87 per cent. NH_3.

The analyses lead to the formula

$$4MoO_3.2PtO_2.2(NH_4)_2O + 19aq.,$$

which requires:

		Calculated.	Found.
$4MoO_3$	576	40.03	39.56
$2PtO_2$	453	31.48	31.63
$4NH_3$	68	4.72	4.91 4.87
$19H_2O$	342	23.77	23.97
	1439	100.00	

As in the last case the molybdic oxide is estimated by difference which in the present state of our knowledge of analysis is the most accurate method. The salt can hardly have been absolutely pure. Water decomposes it and gives an opaque buff-yellow compound which I have not examined. It will be seen from the above that the platino-molybdates described do not correspond, in general composition, with the only silico-molybdates known in which the ratio of molybdic to silicic oxide is as 12 : 1.

Rammelsberg[1] has described a molybdate of the dioxide and ammonium which has the formula

$$4MoO_3.2MoO_2.(NH_4)_2O + 9aq.$$

In endeavoring to prepare a class of stanno-tungstates I obtained a sodium salt the solution of which gave, on evaporation, a hard, nearly colorless, glassy mass. This gave, on analysis, results which did not correspond very well, but the mean of several led to the formula

$$4WO_3.2SnO_2.Na_2O + 7aq.$$

The compound deserves further study, and is not without interest in connection with the two salts noticed above.

60:1:10 *Platino-molybdate of Potassium.*—This salt was obtained by boiling potassic molybdate with an excess of potassic hydrate, and adding a solution of $PtCl_4H_2$ until platinic hydrate which at first dissolves as fast as formed, was in small excess. Acetic acid was then added to an acid reaction. On standing, fine granular yellow crystals were formed in quantity. These were dissolved in hot water and recrystallized. Of this salt:

0.5191 gram gave 0.0098 gram Pt = 2.20 per cent. PtO_2.
0.5191 gram gave 0.5665 gram MoS_3 = 81.85 per cent. MoO_3.
0.6459 gram lost on ignition with WO_4Na_2 0.0447 gram = 6.92 per cent. $O + H_2O = 6.61$ H_2O.
1.2241 grams lost on ignition with WO_4Na_2 0.0872 gram = 7.12 per cent. $O + H_2O = 6.81$ H_2O.

The analyses lead to the formula

$$60MoO_3.PtO_2.10K_2O + 40aq.,$$

which may be written provisionally as

$$12MoO_3.PtO_2.2K_2O.4H_2O + 4\{12MoO_3.2K_2O.3H_2O\} + 24aq.$$

The formula requires:

		Calculated.	Found.
$60MoO_3$	8640.0	82.04	81.85
PtO_2	226.5	2.16	2.20
$10K_2O$	994.0	8.97	9.24
$40H_2O$	720.0	6.83	6.61 6.81
	10530.5	100.00	

[1] Ann. der Phys., Pogg., 127, 291.

This salt is readily soluble in hot water without apparent decomposition. It gives a very pale yellow crystalline precipitate with argentic nitrate and a pale greenish-blue precipitate with cupric sulphate, which is soluble in an excess of this last.

Rosenheim has recently described[1] another platino-tungstate with the empirical formula

$$7WO_3.2PtO_2.5Na_2O + 35aq.,$$

and regards it as a double salt,

$$7WO_3.3Na_2O + 2\{PtO_2.Na_2O\} + 35aq.$$

This salt was obtained by boiling normal sodic tungstate, WO_4Na_2, in concentrated solution with platinic hydrate, and presented small yellow needles which could not be recrystallized without decomposition. He did not succeed in obtaining platino-tungstates by boiling platinic hydrate with various meta-tungstates, and suggests that the three salts which I described in my preliminary notice were mixtures of meta-tungstates (para-tungstates) and platinic oxide. They were, on the contrary, perfectly well defined and crystallized, as were also the platino-tungstates and platino-molybdates described in this paper. Further investigation will probably show that a number of other salts can be obtained by the method which I have described in which the platinic hydrate is brought in contact with acid tungstates or molybdates in the nascent state. Phospho-platino-tungstates and similar molybdenum compounds appear also to exist. A solution of 24 : 1 : 2 phospho-tungstate of sodium readily dissolves platinic hydrate on boiling, and gives an orange-colored solution which after filtration and evaporation deposits ill-defined orange crystals. When a solution of ammonic chloride is mixed with the solution obtained as above, a beautiful orange crystalline salt is thrown down. In a preliminary notice published in 1877,[2] I described the preparation and properties of platino-tungstates having respectively the formulas

$$10WO_3.PtO_2.4Na_2O + 25aq\,;\quad 10WO_3.PtO_2.4K_2O + 9aq.;$$
$$10WO_3.PtO_2.4(NH_4)_2O + 12aq.;$$

[1] Ber. d. chem. Ges., **24**, 2397.

[2] Ber. d. chem. Ges., **10**, 1384; Am. J. Sci., [3], **14**, 61.

and of a platino-molybdate with the formula

$$10MoO_3.PtO_2.4Na_2O + 29aq.$$

All of these tungstate compounds were obtained by boiling

$$10WO_3.4Na_2O + 23aq.$$

with the soluble form of platinic hydrate. The molybdenum compound was obtained in a similar manner, but I am not now able to state what acid molybdate of sodium was employed. I have not succeeded in obtaining these compounds a second time, and in the long interval of time which has elapsed since the publication of my preliminary notice the notes of description and analyses have been lost. I can only express my conviction that more extended investigations will show that no error has been made, and that the compounds unite as described. I will further remark, that, taking the analyses which I have given in this paper, it may be possible to give simpler formulas for some at least of the salts described. The formulas given, represent, I believe, most accurately the results of the analyses, but as the percentages of platinum are relatively small the quotients of these percentages by the atomic mass of platinum are very small divisors. On the other hand, the quotients obtained by dividing the percentages of tungstic or molybdic oxide by the molecular masses of tungstic or molybdic oxide are relatively very large, and the ratio between the two quotients in question becomes somewhat uncertain. The compounds which I have obtained by the method which I have given of bringing platinic oxide *in statu nascenti* into contact with the solutions of acid tungstates or molybdates gives such well-defined and beautifully crystalline salts that the subject will doubtless attract the attention of other chemists. I will make the suggestion that possibly the salts which I described in my preliminary notice may be obtained by adding ammonic chloride to the solutions of the double salts described in this paper, so as, in the case of the tungstic compounds at least, to precipitate the tungstic oxide not combined with platinic oxide in the form of

$$10WO_3.4Na_2O + 4\{10WO_3.4(NH_4)_2O\} + 50aq.,$$

or an analogous salt. The solution should then contain only

a platino-tungstate. The application to the platino-molybdates described is less probable.

Second Series of Pyrophospho-Tungstates and Pyrophospho-Molybdates.

When sodic pyrophosphate is added in excess to a solution containing a metallic salt, the precipitate which is at first found is, in many cases, redissolved with formation of a double salt of sodium and the metal in question. In a certain number of cases, the heavier metal in the new compound is not replaceable under ordinary conditions, and does not exhibit characteristic reactions with tests. These facts are, of course, familiar to all chemists. Persoz supposed that these salts might be represented, in the case of divalent metals, by the general formula, as we should now write it,

$$P_2O_7R'' + P_2O_7Na_4,$$

and that the group P_2O_7R'' was to be regarded as electro-negative to the group $P_2O_7Na_4$, so that the compound would be simply analogous to ClNa. If we write the double salt $P_2O_7R''Na_2$, we may regard the complex P_2O_7R'' as playing the part of a relatively electro-negative group, as in the case of double cyanides, so called. Whether this view is to be considered as identical with that of Persoz, is a question about which opinions may differ, and which is not important for my present purpose. Admitting that the groups P_2O_7R'' or P_2O_7R''' are transferable as such in their relatively simple alkaline salts, we may inquire whether they enter into the composition of complex acids and if so, whether the compounds so formed differ from ordinary pyrophospho-tungstates and pyrophospho-molybdates. As the initial point in this investigation, I have selected mangano-disodic pyrophosphate, $P_2O_7Mn_2Na_2$.

Mangano-sodic Pyrophospho-Molybdate.

In another part of this memoir I have described several salts belonging to the group of pyrophospho-tungstates. As these were peculiar in their constitution, it became a matter of interest to determine whether the pyrophospho-molybdates had a similar constitution, or, in other words, whether they

contained the pyrophosphoric group $22RO_3.9P_2O_5$ found in the salts of the tungstic series.

Molybdic tetroxide boiled with sodic pyrophosphate, care being taken to keep the oxide in excess, is dissolved with much facility, and in large quantity. The colorless solution may be evaporated to a syrup without yielding crystals on standing, and gives no precipitates with salts of potassium or ammonium. The solution, however, gives precipitates with salts of most of the heavier metals. Of these I selected the manganous compounds for special study, supposing that all the manganese would be present as base, and that a comparison could be made between salts of this type and those in which manganese exists in the pyrophosphoric molecule, and which I shall describe further on.

When a solution of manganous chloride is mixed with one of sodic pyrophospho-molybdate prepared as above, a dull buff-colored, apparently amorphous, precipitate is formed. On standing, with an excess of the sodium salt, this was gradually converted into a mass of beautiful bright yellow crystals. These were well washed with cold water, and then dissolved in boiling water. The filtered solution gave, on cooling, a mass of sulphur-yellow crystals, which were again dissolved and recrystallized. The salt was then dried on woolen paper. It was analyzed by Mr. G. W. Patterson.

1.3289 grams gave 0.1065 gram $P_2O_7Mg_2$ = 5.13 per cent. P_2O_5.
1.3289 grams gave 0.2486 gram $P_2O_7Mn_2$ = 9.36 per cent. MnO.
0.9538 gram gave 0.1819 gram $P_2O_7Mn_2$ = 9.53 per cent. MnO.
0.9538 gram gave 0.5934 gram $P_2O_5 + MoO_3$ = 62.22 per cent.
1.0960 grams lost with Wo_4Na_2 0.2037 gram = 18.56 per cent.
0.9445 gram lost with Wo_4Na_2 0.1743 gram = 18.45 per cent.

The analyses lead to the formula

$$22MoO_3.2P_2O_5.7MnO.9Na_2O + 57aq.$$

which requires:

		Calculated.		Found.	
$22MoO_3$	3168	57.26	62.39	57.16	62.29
$2P_2O_5$	284	5.13		5.13	
$7MnO$	497	8.99	19.07	9.36	19.20
$9Na_2O$	558	10.08		9.84	
$57H_2O$	1026	18.54		18.58	18.45
	5533	100.00			

The salt is nearly insoluble in cold water. Boiling water dissolves it, but the salt is decomposed, giving a pale yellow flocky precipitate and a sherry-wine colored solution. On standing a short time, the solution, as it cools, becomes pale yellow, and finally almost colorless, while the precipitate gradually becomes brighter yellow and crystalline, and the original salt appears to be again formed by recombination. Both the precipitate formed in the decomposition by boiling water and the wine-yellow solution, give reactions with argentic nitrate which differ from one another, as well as from the yellow crystalline silver salt formed by digesting the pyrophospho-molybdate of manganese and sodium with argentic nitrate.

In the analysis, the solution of the salt was boiled with mercurous nitrate and mercuric oxide. The precipitate contained only molybdic and phosphoric oxides, and was free from manganese. There is, therefore, reason for assuming, as I have done, that all the manganese is basic, and that none is present in the form of the molecule P_2O_7Mn.

Mangano-ammonic Pyrophospho-Molybdates.

When manganous pyrophosphate is digested for some time with a strong solution of 14:6 acid ammonic molybdate, a buff-yellow, very slightly soluble, compound is formed. This is to be well washed, dried on woolen paper, and afterward *in pleno* over sulphuric acid. Of this salt, analyzed by Mr. G. W. Patterson,

0.7830 gram lost on ignition with WO_4Na_2 0.0778 gram $NH_3 + H_2O = 9.94$ per cent.

0.6554 gram lost on ignition with WO_4Na_2 0.0645 gram $NH_3 + H_2O = 9.84$ per cent.

0.8590 gram gave 0.0338 gram $NH_3 = 3.92$ per cent.

0.7191 gram gave 0.0285 gram $NH_3 = 3.97$ per cent.

{ 0.8725 gram gave 0.0881 gram $P_2O_7Mg_2 = 6.46$ per cent. P_2O_5.
{ 0.8725 gram gave 0.2841 gram $P_2O_7Mn_2 = 12.62$ per cent. MnO.

The analyses lead to the formula

$$20MoO_3.2P_2O_5.10MnO.5(NH_4)_2O + 10aq.,$$

which requires:

		Calculated.		Found.	
$20MoO_3$	2880	66.76	73.34	67.27	73.73
$2P_2O_5$	284	6.58		6.46	
$10MnO$	710	16.46		16.30	
$10NH_3$	170	3.94		3.92 3.97	
$15H_2O$	270	6.26		5.94	
	4314	100.00			

In the analyses the salt was digested for some time at a boiling heat with mercurous nitrate and mercuric oxide. The mercurous salt formed contained manganous oxide. The precipitate was fused with a mixture of potassic and sodic carbonates to separate manganous oxide. The filtrate from this last gave the phosphoric pentoxide. Molybdic tetroxide was determined by difference. As the salt could not be recrystallized, the defects in the analysis are doubtless chiefly due to traces of impurity. The formula of the salt should be written, according to my view:

$$20MoO_3.2P_2O_5.Mn.2(NH_4)_2O.8MnO.3(NH_4)_2O + 12aq.$$

We may have here a double salt, as, for instance,

$$10MoO_3.P_2O_5Mn(NH_4)_2.4MnO.(NH_4)_2O.H_2O + 10MoO_3.P_2O_5Mn(NH_4)_2.4MnO.2(NH_4)_2O + 12aq,$$

but of course other arrangements are possible.

The manganese in the molecule containing P_2O_5 may be called, for convenience, the internal or fixed manganese, to distinguish it from the external or basic manganese. To determine, if possible, the ratio between the external and internal manganese, I digested a weighed portion of the salt in the cold for twelve hours with mercurous nitrate, and then boiled, adding a little mercuric oxide in the usual manner. In the filtrate, after separating the mercury, the manganese was determined as $P_2O_5Mn_2$. In this manner,

1.2306 grams gave 0.3520 gram $P_2O_5Mn = 11.08$ per cent.

From this it appears that about $\frac{1}{12}$ of the manganese was precipitated by mercurous nitrate, in place of $\frac{8}{10}$. If, therefore, we consider $\frac{2}{10}$ of the manganese to be present in the salt as P_2O_5Mn, we must suppose that this molecule is broken up, to a certain extent at least, by boiling with mercurous

nitrate, and it is very doubtful whether the manganous oxide exists in any other form than as a base. Certainly there is no sufficient evidence that it forms here an integrant molecule P_2O_7Mn, as in sodio-manganous pyrophosphate, $P_2O_7Mn.Na_2$. I regard the question, however, as still an open one, since the molecule P_2O_7Mn, assuming its existence, may be decomposed by mercurous nitrate and give a corresponding mercurous integrant molecule $P_2O_7Hg_2$, and since the salt is decomposed by water like the other salts of this series. It appears also from the above that the pyrophospho-molybdates do not correspond in composition to the pyrophospho-tungstates. At least I have not found in them the molybdenum molecule corresponding to the tungstic molecule, $22WO_3.9P_2O_5$. It must, however, be remarked that, as I shall show, the pyrophospho-tungstates which contain manganese do not contain this molecule.

Mangano-sodic Pyrophospho-Tungstates.

These salts are very easily formed by boiling manganous pyrophosphate with acid tungstates. Dark sherry-wine colored solutions are formed, which, in cooling, deposit crystals in abundance.

14 : 1 : 3 : 6 *Mangano-sodic Pyrophospho-Tungstate.* — This salt is formed more conveniently by mixing a solution of 12 : 5 sodic tungstate with manganous pyrophosphate and digesting for some hours in a closed bottle heated in a water-bath. The pyrophosphate must be in excess. It dissolves rather slowly to a fine deep orange-colored liquid, which after evaporation deposits beautiful crystals, which may be redissolved and recrystallized. In spite of the employment of an excess of manganous pyrophosphate, it is rather difficult to obtain a solution of the salt which is perfectly saturated with the manganous salt. The crystals have a brownish-orange color. They effloresce in dry air, though not rapidly, but *in pleno* over sulphuric acid they lose water in relatively large quantity. Of this salt, analyzed by Mr. G. W. Patterson,

1.4176 grams lost on ignition with WO_4Na_2 0.2032 gram = 14.34 per cent. water.

1.2375 grams gave 0.0611 gram $P_2O_7Mg_2$ = 3.16 per cent. P_2O_5.

{ 1.0476 grams gave 0.1041 gram $P_2O_7Mn_2$ = 4.97 per cent. MnO.
1.0476 grams gave 0.7650 gram $WO_3 + P_2O_5$ = 73.05 per cent.

The analyses lead to the formula

$$14WO_3.P_2O_5.3MnO.6Na_2O + 36aq.,$$

which requires:

		Calculated.		Found.	
$14WO_3$	3248	70.25	73.32	69.89	73.05
P_2O_5	142	3.07		3.16	
$3MnO$	213	4.62	12.66	4.97	12.65
$6Na_2O$	372	8.04		7.68	
$36H_2O$	648	14.02		14.34	
	4623	100.00			

We may give this salt the formula

$$14WO_3.6Na_2O + P_2O_5Mn_2 + 36aq.,$$

if we suppose that the pyrophosphate of manganese has become orthophosphate. Both constituents are then normal salts.

The ammonium salt was prepared by double decomposition between the sodium salt and ammonic chloride, and repeated crystallization. It presented orange-colored prismatic crystals, very soluble both in hot and cold water. Of this salt:

0.7846 gram gave 0.01715 gram NH_3 = 2.19 per cent.
0.6556 gram gave 0.01394 gram NH_3 = 2.13 per cent.
0.4886 gram gave 0.0594 gram $NH_4 + H_2O$ = 12.16 per cent.
1.0895 grams gave 0.1162 gram $P_2O_7Mn_2$ = 5.83 per cent. MnO.

The analyses correspond well with the formula

$$28WO_3.2P_2O_5.6MnO.5(NH_4)_2O.2Na_2O + 48aq.,$$

which requires:

		Calculated.	Mean.		
$28WO_3$	6496	77.67	77.76	77.84	77.69
$2P_2O_5$	284	3.40	3.13	3.13	
$6MnO$	426	5.09	5.39	5.33	5.45
$10NH_3$	170	2.03	2.16	2.13	2.19
$2Na_2O$	124	1.48	1.56	1.56 (diff.)	
$48H_2O$	864	10.33	10.00	10.00	
	8364	100.00			

We may formulate this salt as

$$\{14WO_3.4MnO.2Na_2O + P_2O_5Mn_2\} + \{14WO_3.5(NH_4)_2O.H_2O + P_2O_5H_4\} + 45aq.,$$

the type being $14WO_3.6.RO + P_2O_5R'_4$, so that so far as the empirical constitution is concerned the salt may be regarded as a double salt of two normal constituents. The analyses were made by Mr. G. W. Patterson.

[*To be continued.*]

DIAZOBENZENE ANILINE CHLORIDE.

By J. H. Kastle and B. C. Keiser.

In the hope of obtaining diazobenzene chloride it occurred to one of us (Kastle), some years ago, to try the action of nitrosyl chloride upon aniline hydrochloride. Several experiments were made with these reagents, as a result of which a substance containing chlorine was obtained which, in many espects, resembled the other salts of diazobenzene. Notwithstanding the promise of these preliminary experiments, the investigation could not be carried out at that time and it was not until last summer that work along this line could be resumed. We have obtained as the result of our study of this reaction, not diazobenzene chloride, but a double salt of the same with aniline hydrochloride—that is, a compound whose composition and nature are probably to be represented by the formula $C_6H_5.N_2.Cl : ClH_3N.C_6H_5$.

Such a conclusion, we believe, to be warranted by the following observations:

Action of Nitrosyl Chloride on Aniline Chloride.

Nitrosyl chloride, prepared in the usual manner by treating nitrosyl sulphate with perfectly dry common salt, was passed into a thick paste of aniline hydrochloride and water. The vessel containing the mixture was surrounded by a freezing mixture of ice and salt. It was found that under these conditions action took place readily between the nitrosyl chloride and aniline hydrochloride, the latter going into solution in the

small quantity of water present, forming a dark, dirty-green or reddish-brown solution. The solution thus obtained was found to undergo decomposition very readily—so readily that in but few instances was it found expedient to pass in the quantity of gas required by the theory; and when this was done the yield was much smaller than from those batches which were exposed to smaller quantities of the gas. The best results were obtained with from one-half to two-thirds the theoretical quantity of nitrosyl chloride.

The solution obtained as above described was mixed with about an equal quantity of cold absolute alcohol and cold absolute ether added in small quantities at a time. After each addition of ether the vessel containing the substance was shaken while surrounded with cracked ice. After a time a white crystalline precipitate made its appearance which was found to increase in bulk up to a certain limit with each fresh portion of ether added. The precipitate was filtered off with the aid of a pump and washed with a small quantity of ether. The substance thus obtained certainly possesses the general characteristics of a diazo-compound. Frequently during the course of the investigation it was obtained in well-defined needle-shaped crystals, which became green, then pink, and, finally, brown in color on exposure to the air. It dissolves freely in water and in alcohol forming green solutions which rapidly change to red upon boiling or standing exposed to the air. The substance explodes when heated to 105° or over, giving off nitrogen and small quantities of hydrochloric acid.

A combustion-analysis of the compound was attempted; owing, however, to the explosions taking place in the tube no satisfactory results could be obtained.

On boiling the compound with water it was observed that only a portion of the nitrogen could be expelled; hence, in order to determine the percentage of this element in the compound, a small quantity of the substance was boiled with water in a small flask from which the air had been expelled by carbon dioxide. The nitrogen thus evolved was collected over caustic potash. The fixed nitrogen was determined as follows: A small portion of the substance was boiled with water in a Kjeldahl flask, the water expelled, and a Kjeldahl determination made of the residue.

The chlorine was determined by the usual gravimetric and volumetric methods. The following are the results for nitrogen and chlorine:

	I.	II.	III.	IV.	Calculated for $C_6H_5N_2Cl$: $ClH_3N.C_6H_5$.
Diazo nitrogen[1]				11.01	10.27
Fixed nitrogen[2]				4.96	5.18
Chlorine	24.85	25.38	25.44	24.91	26.29

The above figures for the nitrogen, together with the fact that two-thirds of the total quantity of this element present is driven off by simply boiling with water while the other one-third is retained, go to prove that the substance is not diazobenzene chloride.

These figures and facts, however, do prove conclusively that the compound contains a diazo residue and also a nitrogenous residue which is not of a diazo nature. The figures for the nitrogen agree fairly well for the double salt $C_6H_5.N_2.Cl = ClH_3N.C_6H_5$. The numbers obtained for the chlorine agree better for diazobenzene chloride than they do for the double salt. The significance of these results will be discussed farther on.

Action of Water on the Compound.

About forty grams of the substance were dissolved in a liter of water and the solution heated to boiling. Decomposition took place very readily and large quantities of nitrogen were evolved. The solution was allowed to cool and was then filtered to remove a small quantity of resinous matter which had been formed during the decomposition. The filtered liquid was rendered decidedly alkaline with caustic soda and shaken up with ether; the ethereal layer was then separated from the alkaline liquid by means of a separating-funnel, and the ether allowed to evaporate spontaneously, whereby a reddish-brown oil having the odor of aniline was obtained. A small quantity of the oil, dissolved in concentrated sulphuric acid and treated with a small crystal of potassium bichromate, gave the magnificent blue color characteristic of aniline. The

[1] By "diazo nitrogen" is meant that portion expelled as free nitrogen on boiling the compound with water.

[2] By "fixed nitrogen" is meant that portion remaining in the compound after expulsion of the diazo nitrogen.

greater portion of the oil was treated with hydrochloric acid. The highly colored chloride thus obtained was purified with animal charcoal and recrystallized from water. It was finally obtained in colorless transparent crystals which gave the following numbers for chlorine on analysis:

	Found.	Calculated for $C_6H_5.NH_2.HCl$.
Cl	27.49 per cent.	27.41

The alkaline fluid left after separation of the ethereal layer containing the aniline, was then acidified with hydrochloric acid and again extracted with ether; the ether was separated as above and allowed to evaporate spontaneously. There was left behind an oily substance having the general characteristics of phenol. It responded to the usual tests for phenol with ferric chloride, etc., and on treatment with nitric acid it gave othonitrophenol which was identified by its color, odor, and melting-point.

By decomposition with water, therefore, the compound obtained by the action of nitrosyl chloride on aniline chloride yields phenol and aniline hydrochloride.

The Substance Yields Phenylhydrazine on Reduction.

In view of the fact that phenylhydrazine is very easily prepared by the reduction of a solution of diazobenzene chloride with stannous chloride, we were naturally led to try the action of stannous chloride upon a solution of the new compound. 5-10 grams of the substance were dissolved in a small quantity of water, and to this solution, kept cold by surrounding the flask containing it with cracked ice, was added the theoretical quantity of stannous chloride dissolved in concentrated hydrochloric acid. Immediately upon mixing these solutions the mass became solid. In order to remove the small quantity of liquid adhering to the crystals the mass above obtained was filtered. The residue was mixed with water, treated with an excess of caustic soda, and extracted with ether. The ether extract was allowed to evaporate spontaneously, whereby a reddish-brown oil was obtained which was then treated with an excess of concentrated hydrochloric acid. Two chlorides were thus obtained, one soluble, the other

insoluble, in an excess of the concentrated acid. The latter was purified by dissolving in a small quantity of water and reprecipitating with concentrated hydrochloric acid. The substance was thus obtained in the form of beautiful pearly white crystals identical in appearance, solubility in water and concentrated hydrochloric acid, and in chemical conduct with phenylhydrazine hydrochloride. Dilute aqueous solutions of it were found to reduce solutions of gold, platinum, silver, and mercury salts with remarkable ease.

The other chloride formed in this reduction, *viz.*, the one soluble in concentrated hydrochloric acid, was recovered and shown to be aniline hydrochloride. Hence, by reduction of the new compound with stannous chloride, phenylhydrazine hydrochloride and aniline hydrochloride are obtained.

The Substance Forms a Double Salt with Platinum Chloride.

A concentrated aqueous solution of the new diazo derivative was treated with a strong solution of platinum chloride containing a small quantity of concentrated hydrochloric acid. A beautiful double salt was thus obtained in the form of golden-yellow crystals. In order to determine the platinum a weighed quantity of the substance was heated in a covered platinum crucible and the spongy platinum weighed. It gave the following result:

	Found.	Calculated for $C_6H_5.N_2.Cl.ClH_3N.C_6H_5.PtCl_4$.
Pt	32.15	32.12

Synthesis of the Compound by Means of Diazobenzene Chloride and Aniline Hydrochloride.

In view of the fact that both the decomposition of the compound by water and its reduction by means of stannous chloride indicate that it contains a diazobenzene and an aniline residue it was thought that possibly the substance might be prepared synthetically by bringing together solutions of diazobenzene chloride and aniline hydrochloride, containing the required quantities of each of these substances. In order to test the correctness of this supposition the following experiment was tried: 9 grams of aniline hydrochloride were dis-

solved in the smallest possible amount of water and to this solution, well cooled by a freezing-mixture, there was added the theoretical quantity of a concentrated solution of potassium nitrite and also hydrochloric acid. About 20 cc. of absolute alcohol were then added together with about the same quantity of ether. The potassium chloride which was thus precipitated was removed by filtration, and to the filtrate containing the diazobenzene chloride there were added 9 grams of aniline hydrochloride in solution in water and alcohol. Cold absolute ether was then added in small quantities at a time as long as any precipitate was produced.

There was obtained in this way quite a quantity of a substance identical in every respect with that obtained by the action of nitrosyl chloride on aniline hydrochloride. When first obtained, the substance is white, rapidly passing on drying through complimentary shades of green and pink. It dissolves freely in water giving a pale green solution which rapidly changes to red on boiling, with evolution of nitrogen when heated to 105° or over, the dry substance explodes with evolution of nitrogen and small quantities of hydrochloric acid gas. On analysis it gave the following numbers for nitrogen and chloride:

	Found.	Calculated for $C_6H_5.N_2.Cl:ClH_3N.C_6H_5$.
Diazo nitrogen	10.88	10.27
Fixed nitrogen	4.68	5.18
Chlorine	25.13	26.29

The above numbers for the nitrogen agree fairly well with those demanded by the theory. The want of exact agreement in the case of the chlorine is doubtless to be accounted for partly by the fact that, on standing, the compound undergoes a slight decomposition whereby a small quantity of hydrochloric acid escapes. This was proven by allowing a small quantity of the substance to remain for some time in moist air; the substance was found to deliquesce and silver nitrate gave a marked turbidity when shaken with the air in which the substance had been allowed to stand. Again, the formation of any benzene chloride—and it is more than probable that this substance would be formed by the spontaneous

decomposition of the compound—would cause a decrease in the quantity of chlorine obtained by the usual methods of simple precipitation with silver nitrate.

On Treatment with Caustic Potash the Substance Yields Diazoamidobenzene.

Another line of proof regarding the nature of the substance here at hand remained to be tested. It is well known that diazoamidobenzene is usually prepared by treating a salt of diazobenzene with aniline; hence if this compound contains both a diazobenzene and an aniline residue it ought to yield diazoamidobenzene when treated with one molecule of caustic potash, thus:

$$C_6H_5.N_2.Cl : C_6H_5.NH_2Cl + KOH = C_6H_5.N_2.Cl + C_6H_5.NH_2 + KCl + H_2O;\quad C_6H_5.N_2.\underline{Cl} + H\underline{HN}.C_6H_5 = HCl + C_6H_5.N_2.HN.C_6H_5.$$

In order, therefore, to determine the possibility of such a reaction as this with the new compound several grams of the substance, prepared by the action of nitrosyl chloride upon aniline chloride, were dissolved in water and treated with the required quantity of caustic potash. Action took place at once, and a brownish-yellow precipitate was obtained which, on purification with animal charcoal and recrystallization from alcohol, was obtained in yellow crystals. It was found to be almost insoluble in water and readily soluble in hot alcohol from which it crystallized on cooling. It melted at 97° (uncorrected). So close is the agreement between the properties observed for this substance and those of diazoamidobenzene as usually prepared that there can be no doubt as to its identity with diazoamidobenzene.

Similar results were reached by treating the compound made from diazobenzene chloride and aniline hydrochloride with caustic potash.

Conclusion Regarding the Nature of the Substance.

As shown in the above the following points have been clearly established regarding the nature of the substance herein described:

1. It yields phenol and aniline chloride on decomposition with water.

2. It yields phenylhydrazine and aniline hydrochloride on reduction with stannous chloride.

3. It yields diazoamidobenzene on treatment with one molecule of caustic potash.

4. It has the general appearance and properties of a diazo compound. It changes color on drying and explodes when rapidly heated. It is not as explosive, however, as the salts of diazobenzene.

5. On boiling with water it gives off two-thirds, and only two-thirds, of its nitrogen.

6. It yields a crystalline platinum double salt with platinum chloride, containing 32.15 per cent. of platinum.

7. The substance itself can be prepared after the manner of double salts. (See p. 95.)

In the light of these facts we have been led to regard this compound as a double chloride of diazobenzene and aniline, and to call it diazobenzene-aniline chloride. It would certainly seem reasonable to suppose that a double salt of this nature, $C_6H_5.N_2.Cl:ClH_2N.H_5C_6$, could be prepared by the method described on p. 95; and that, in all probability, it would conduct itself towards water, reducing agents, and caustic potash as did the substance above described.

Some few attempts have been made to obtain analogous derivatives with the toluidines, without success. It is hoped, however, that by further study we may be able to obtain other double salts of this nature.

STATE COLLEGE OF KENTUCKY, LEXINGTON,
December, 1894.

Contributions from the Kent Chemical Laboratory of the University of Chicago.

ON IMIDO-ETHERS OF CARBONIC ACID.

BY FELIX LENGFELD AND JULIUS STIEGLITZ.

In the course of an investigation on the action of phosphorus pentachloride on phenylurethane,[1] we found that ethylanilidochlorformate treated with dry hydrochloric acid gives ethyl chloride and chlorformanilide. Certain reac-

[1] This Journal, 16, 70.

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tions[1] made us think that probably hydrochloric acid was first added:

$$Cl.C\begin{matrix}\diagup NC_6H_5\\ \diagdown OC_2H_5\end{matrix} + HCl = C_6H_5NH.C\begin{matrix}\diagup Cl\\ \diagdown O\end{matrix}\!\!\begin{matrix}Cl\\ C_2H_5\end{matrix}$$

and that the addition-product decomposed as indicated. This is one of a number of reasons for suspecting that the chlorides of the imido-ethers, which suffer this same decomposition on heating, more or less, may not have the constitution RC(OR)(NRHCl) usually ascribed to them, but RCCl(NHR)(OR).

We were unable to isolate the supposed intermediate chloride of ethylanilidochlorformate as it seemed to decompose even at—15°. To further test the above view we have tried the action of hydrobromic acid on ethylanilidochlorformate and of hydrochloric acid on ethylanilidobromformate. This allowed us to follow closely the course of the halogen atom originally in the ether and of that originally in the acid. In both reactions the intermediate products would be the same, if our views proved correct, and probably would show a behavior allowing this to be recognized.

$$ClC(NC_6H_5)OC_2H_5 + HBr = ClBrC(NHC_6H_5)OC_2H_5$$
$$BrC(NC_6H_5)OC_2H_5 + HCl = ClBrC(NHC_6H_5)OC_2H_5$$

Bromformanilide, $BrCONHC_6H_5$.—Qualitative tests showed that, when dry hydrobromic acid gas acts on ethylanilidochlorformate, both ethyl chloride and bromide are given off, leaving a mixture of chlorformanilide and bromformanilide. As the latter had never been obtained, we prepared some of the pure substance by passing dry hydrobromic acid over freshly distilled phenyl isocyanate:

$$C_6H_5NCO + HBr = BrCONHC_6H_5.$$

The gas is rapidly absorbed, crystals being formed on the surface; to melt this crust and complete the reaction, the mixture is repeatedly warmed to 50°–60° in the current of the gas. By powdering under dry petrolic ether, filtering, washing with petrolic ether, and bringing on a clay plate into a vacuum desiccator, white crystals of bromformanilide were

[1] *Ibid*, 75, 76.

obtained. It has the same penetrating odor of phenyl isocyanate as chlorformanilide, melts at 67° (heated rapidly) and decomposes at 85°–100° into hydrobromic acid and phenyl isocyanate.

Analysis.—0.2805 gram substance (heated with lime) required 14 cc. $\frac{N}{10}$ $AgNO_3$ solution (Volhard).

	Calculated for C_7H_6NOBr.	Found.
Br	40.00	39.93

As it was essential to know whether hydrochloric acid converts bromformanilide into chlorformanilide giving hydrobromic acid:

$$C_6H_5NHCOBr + HCl = C_6H_5NHCOCl + HBr,$$

one gram of freshly prepared bromformanilide dissolved in 7.5 cc. cold absolute ether, was treated with 2.5 cc. ethereal hydrochloric acid (7.5 per cent. solution). After twenty minutes the ether was evaporated in a vacuum, the residue washed with a little ligroin and dried as usual. 0.241 gram substance heated with lime required 11.68 cc. $\frac{1}{10}$ N- silver nitrate.

Calculated for C_7H_6NOCl.	Calculated for C_7H_6NOBr.	Found.
15.5 cc.	12.05 cc.	11.68 cc.

Freshly prepared chlorformanilide treated in the same way with ethereal hydrobromic acid gave:

0.32715 gram silver halide obtained after combustion with lime, was reduced, giving 0.2444 gram silver.

	Calculated for AgCl.	Calculated for AgBr.	Found.
Ag	75.26	57.44	74.71

Both of these experiments show that there is practically no action under these conditions.

In order to obtain ethylanilidobromformate as required for this work, we first prepared:

Phenylimido-carbonyl Bromide, $C_6H_5N:CBr_2$.—Nef[1] found that phenyl isocyanide absorbs bromine, probably forming the compound, but did not examine the product any further. It can be obtained as follows: 10 grams (1 molecule) phenyl isocyanide, freshly distilled in a

[1] Ann. Chem. (Liebig), **270**, 270.

vacuum, was dissolved in about 70 cc. of chloroform, from which every trace of water and alcohol had been carefully removed. The solution was cooled to—10° and 15.5 grams bromine (1 molecule), dissolved in 3 to 4 volumes of chloroform slowly added through a dropping funnel. A sudden change of color from blue to brownish-green took place when the calculated amount of bromine had been added and marked the end of the reaction. After twenty minutes, the chloroform was distilled off in a fractionating bulb under diminished pressure at 30°–40° in a current of dry air. The oily residue distills without decomposition in a vacuum. The temperature rapidly rose to 123° and then very soon to 128°–128.5° where it remained constant (at 20 mm.) during the greater part of the operation. An orange-colored oil distilled without any apparent decomposition, just as in distilling phenylimido carbonyl chloride, the cork was slightly attached, and probably caused the coloration. After refractionating, the portion boiling at 127° at 18 mm. was analyzed.[1]

0.1910 gram gave 0.2577 gram silver bromide.

	Calculated for $C_7H_5NBr_2$.	Found.
Bromine	60.83	57.42

Phenylimidocarbonyl bromide has an odor similar to that of phenylimidocarbonyl chloride, but acquires easily a faint odor of phenyl isocyanide as well. It was converted by means of sodium ethylate into:

Ethylanilidobromformate, $C_6H_5N : CBr(OC_2H_5)$. — Phenylimidocarbonyl bromide (1 molecule) was treated with (1 molecule) sodium ethylate in absolute alcoholic solution just as described by us[2] for treating phenylimidocarbonyl chloride. An oil was finally obtained which was at first slightly reddish but soon became darker. It had an odor like ethylanilidochlorformate, but also a strong odor of phenyl isocyanide. By warming to 90°–95° at 17 mm. most of the isocyanide was distilled off. On attempting to distill the oil remaining, it decomposed largely into ethyl bromide and phenyl isocyanate. As this prevented the purification of the ethylanilidobromformate for analysis, we determined the nature of the main part

[1] NOTE.—Analysis made according to Carius by W. R. Smith.

[2] This Journal, 16, 73.

of the product as follows: Heat decomposes it into phenyl isocyanate and ethyl bromide, just as the corresponding chlorine compound gives phenyl isocyanate and ethyl chloride.[1]

$$C_6H_5N:C<_{O}^{Br}{}_{C_2H_5} \qquad C_6H_5N:C<_{O}^{Cl}{}_{C_2H_5}$$

and hydrobromic acid gives ethyl bromide and bromformanilide:

$$C_6H_5N:CBr(OC_2H_5)+HBr=C_2H_5Br+C_6H_5.NH.CO.Br.$$

As will be seen below, for our purposes there was no objection to the use of the crude product. Sodium alcoholate acts, as shown, partly according to the equation,

$$C_6H_5N:CBr_2+NaOC_2H_5=C_6H_5N:CBr(OC_2H_5)+NaBr,$$

and partly removes bromine, regenerating phenyl isocyanide,

$$C_6H_5NCBr_2-Br_2=C_6H_5N:C.$$

On treating phenylimidocarbonyl bromide with aqueous sodic hydrate, a strong odor of phenyl isocyanide is also evolved. The bromide appears to be less stable than the chloride.

Action of Hydrobromic Acid on Ethylanilidochlorformate.—To 1.5 gram (1 molecule) of ethylanilidochlorformate dissolved in absolute ether was added an equivalent quantity of ethereal hydrobromic acid (1 molecule) in a freezing-mixture. After thirty minutes the ether was removed by the vacuum pump at 0°, and the residue treated with dry petrolic ether, filtered, washed rapidly, and placed on a clay plate in a vacuum desiccator. An analysis of the haloformanilide, $XCONHC_6H_5$, showed that it was chlorformanilide.

Analysis.—Some of the substance was heated with lime, which was dissolved in nitric acid and treated with silver nitrate; a weighed quantity of the silver halide obtained, was reduced to silver. 0.2359 gram silver halide gave 0.1776 gram silver.

	Calculated for AgCl.	Found.
Ag	75.26	75.285

The reaction that took place is:

$$C_6H_5N:CCl(OC_2H_5)+HBr=C_6H_5NHCOCl+C_2H_5Br.$$

[1] This Journal, 16, 74.

Qualitative tests having shown that, in the action of gaseous hydrobromic acid on ethylanilidochlorformate ethyl chloride, ethyl bromide, chlor- and bromformanilide are formed, the quantitative course of the action was determined by estimating the proportion of ethyl chloride and bromide as follows: Freshly distilled ethylanilidochlorformate was used, prepared as described in our previous paper and having the boiling-point 103°–104° at 17–18 mm.[1] The hydrobromic acid used was previously prepared from bromine, red phosphorus, water and potassium bromide and collected over mercury in bottles. For the determination it was, by means of mercury, made to pass in a slow current through a long calcium chloride tube and then into a small tube containing about one gram of the ethylanilidochlorformate, which was kept immersed in cold water. The gases then passed through a short tube containing calcium chloride and then through two sets of Geissler's bulbs containing a ten per cent. solution of sodic hydrate tinged with methylorange and into a narrow combustion tube, about twenty inches long, filled with calcium oxide and heated to redness. A moderate excess of hydrobromic acid was used and then dry air slowly passed through the system for an hour while the bulbs of the Geissler apparatus were heated in water-baths to about 90°. In this way all the alkyl halide formed, and no other halogen compound passed into the combustion tube. The lime was dissolved in nitric acid, the halogens precipitated as silver halide and a weighed quantity of this reduced to silver, and from this the proportion of ethyl chloride and ethyl bromide calculated. The results are those of two different determinations.

Analysis.—I. 0.4971 gram silver halide gave 0.3366 gram silver, corresponding to 57.62 per cent. AgCl and 42.38 per cent. AgBr, *i. e.*, 10 molecules of ethyl bromide to 18 molecules ethyl chloride.

II. 0.4486 gram silver halide gave 0.3112 gram silver, corresponding to 66.93 per cent. AgCl and 33.07 per cent. AgBr, *i. e.*, 10 molecules of ethyl bromide to 26 molecules of ethyl chloride.

[1] In our first paper, This Journal, **16**, 74, the boiling-point was given by mistake as 115°–120° at 20 mm.; it should have been 105°–106°.

Action of Hydrochloric Acid on Ethylanilidobromformate.—As the purpose of this investigation only required the quantitative determination of the proportion of ethyl chloride and ethyl bromide evolved in this action, and our system of apparatus only allowed the alkyl halides to pass into the lime tube, we could use the crude ethylanilidobromformate from which most of the phenyl isocyanide had been removed in a dry current of air at 100° at 20 mm., and which contained as impurities, only polymerized phenyl isocyanide and traces of the isocyanide itself. The experiment was conducted just as described in the analogous reaction.

Analysis.—I. 0.36625 gram silver halide gave 0.21175 gram silver, corresponding to 98 per cent. silver bromide and 2 per cent. silver chloride, or 1 molecule of ethyl chloride to 37 molecules ethyl bromide.

II. 0.155 gram silver halide gave 0.0893 gram silver, corresponding to 99.05 per cent. silver bromide and 0.95 per cent. silver chloride, or 1 molecule of ethyl chloride to 80 molecules of ethyl bromide. Therefore, what is given off is essentially ethyl bromide.

We see that the action of hydrobromic acid on ethylanilidochlorformate depends apparently on the conditions; in ethereal solution we have chiefly:

I. $C_6H_5N:CCl(OC_2H_5)+HBr=C_6H_5NHCOCl+C_2H_5Br$;

and with gaseous hydrobromic acid, besides I, to a somewhat greater extent also:

II. $C_6H_5N:CCl(OC_2H_5)+HBr=C_6H_5NHCOBr+C_2H_5Cl$.

Hydrochloric acid gas acts on ethylanilidobromformate almost entirely according to:

III. $C_6H_5N:CBr(OC_2H_5)+HCl=C_6H_5NHCOCl+C_2H_5Br$;

and to a slight extent according to:

IV. $C_6H_5N:CBr(OC_2H_5)+HCl=C_6H_5NHCOBr+C_2H_5Cl$.

From these reactions the following conclusions may be drawn:

1°. From II and III giving the main actions we see there is *not* a simple removal of the alkyl by the acid according to:

V. $(C_6H_5N)XC.O\,C_2H_5+YH=C_6H_5NHCOX+C_2H_5Y$.

2°. The intermediate product, probably formed, can not

have the constitution $\begin{matrix}H\\Y\end{matrix}\!>\!NC_6H_5:C<\!\begin{matrix}X\\OC_2H_5\end{matrix}$ usually ascribed to the halides of imido-ethers since, in the first place, according to reaction III:

VI. $\begin{matrix}H\\Cl\end{matrix}\!>\!NC_6H_5:C<\!\begin{matrix}Br\\O\,C_2H_5\end{matrix}$ would give $\begin{matrix}H\\Cl\end{matrix}\!>\!NC_6H_5:C:O$

as the constitution of chlorformanilide (a so-called "urea-chloride"), whereas it is better expressed[1] by $C_6H_5NHCOCl$; —and since, in the second place, the loss of alkyl halide, taking place in the same way as the loss of alkyl chloride from the salts of the imido-ethers $RC=\begin{matrix}NRH\ X\\O\,C_2H_5\end{matrix}$ would give us for II:

VII. $ClC=\begin{matrix}NC_6H_5H\ Br\\O\,C_2H_5\end{matrix}=C_2H_5Br+ClCONHC_6H_5$ chlor-formanilide and ethyl bromide, while in fact the products with gaseous hydrobromic acid (equation II) are chiefly brom-formanilide and ethyl chloride. Just so in III:

VIII. $BrC=\begin{matrix}NC_6H_5H\ Cl\\O\,C_2H_5\end{matrix}=ClC_2H_5+BrCONHC_6H_5$ would give us bromformanilide and ethyl chloride, while the actual products are nearly entirely ethyl bromide and chlorform-anilide.

3°. The formation of the intermediate addition-product, $C_6H_5NH.C(OC_2H_5)ClBr$, explains perfectly both the forma-tion of haloformanilide of the constitution C_6H_5NHCOX, and the formation of the alkyl halides as actually found. We obtain then by the action of hydrobromic acid on ethylanilido-chlorformate, and of hydrochloric acid on ethylanilidobrom-formate, the same addition-product which can decompose according to:

IX. $C_6H_5NHC\!\begin{matrix}Cl\\O\,C_2H_5\\Br\end{matrix}=C_6H_5NHCOBr+ClC_2H_5$ or

[1] Leuckart, Ber. d. chem. Ges., **18**, 873; Gattermann, *Ibid*, **20**, 118; and Ann. Chem. (Liebig), **244**, 30.

X. $C_6H_5NHC\begin{matrix}Cl\\ \diagup\\ O\,C_2H_5\\ \diagdown\\ Br\end{matrix} = C_6H_5NHCOCl + C_2H_5Br,$

according to the conditions obtaining in the experiment. With dry hydrobromic acid both IX and X occur. *With dry hydrochloric acid and ethereal hydrobromic acid, practically only reaction X takes place.* The given constitution of the intermediate product agrees best, therefore, with the actual behavior of the compounds, briefly:

1. The formation of the haloformanilides of the constitution C_6H_5NHCOX.

2. The formation in one reaction of both ethyl chloride and bromide, and the two acid anilides, chlor- and bromformanilide.

3. The formation of ethyl bromide only, when only one alkyl halide is given off, whether hydrobromic or hydrochloric acid is used. The question naturally arises why the addition-product, under apparently the same conditions when formed by the action of the dry gases, does not give absolutely identical decomposition-products. The conditions are, however, only apparently the same, and only as to external temperature, etc. The fact that with gaseous acids the halogen of the original ether is given off to a greater extent than the new halogen entering indicates forces at work in the molecule which we cannot subject to exact identity of condition. The conclusions drawn above are based on facts which exist independently of any such requirement.

As we could not isolate the addition-product, which forms so important a link in these reactions, we treated the corresponding phenylanilidochlorformate, $C_6H_5N:CCl(OC_6H_5)$, with gaseous hydrochloric acid in the expectation that the addition-product would not lose phenyl chloride and so would prove more stable. This was found to be so. A product, $C_6H_5NH.CCl_2(C_6H_5)$, was obtained, in perfect agreement with the views expressed above.

Phenoxyformphenylamidodichloride $(C_6H_5O)CCl_2(NHC_6H_5)$. —Phenylanilidochlorformate was prepared from phenylimidocarbonylchloride and sodium phenolate, according to our

method for preparing the ethylate.[1] 1.5 grams phenylanilidochlorformate (M. p. 41°) was dissolved in 30 cc. petrolic ether (B. p. 30°–40°) and filtered from a slight residue of phenyl carbanilate. The filtrate was placed in a freezing-mixture and dry hydrochloric acid passed in. A white precipitate which formed was rapidly filtered, washed with petrolic ether, and brought on a clay plate in a vacuum desiccator.

Analysis.—0.1667 gram substance heated with lime required 12 cc. $\frac{N}{10}AgNO_3$ solution (Volhard).

	Calculated for $C_{13}H_{11}NOCl_2$.	Found.
Cl	26.49	25.58

Phenoxyformphenylamidodichloride (a derivative of orthocarbonic acid), softens at 60° and melts at 65° with decomposition. In the presence of moisture it yields phenyl carbanilate (M. p. 125°). It is formed according to the equation:

$$C_6H_5N:CCl(OC_6H_5)+HCl=C_6H_5NH.CCl_2(OC_6H_5).$$

ADDITION OF HYDROCHLORIC ACID TO CARBODIPHENYLIMIDE.

As we found[2] that carbodiphenylimide unites with ethyl alcohol to form ethylisodiphenylurea,

$$C_6H_5N:C:NC_6H_5+HOC_2H_5=C_6H_5N:C(NHC_6H_5)(OC_2H_5),$$

we thought we could, by means of this compound, decide whether the addition-product of hydrochloric acid to carbodiphenylimide is a salt, $C_6H_5N:C:NC_6H_5.HCl$, or, as seems probable, an imidechloride $C_6H_5N:C<^{Cl}_{NHC_6H_5}$.

Weith first found[3] that carbodiphenylimide, when treated in benzene solution with hydrochloric acid, adds one molecule of the acid. He obtained a crystalline precipitate which a chlorine determination showed to be $(C_6H_5N)_2C.HCl$. Later he states[4] that, on continuing the current of hydrochloric acid, the precipitate redissolved, and the solution, on standing, deposited distinct crystals, which he did not analyze, but took to be larger crystals of the same chloride, and this has passed into

[1] This Journal, **16**, 73; and W. R. Smith, This Journal, **16**, 392.
[2] Ber. d. chem. Ges., **27**, 926. [3] *Ibid*, **7**, 11. [4] *Ibid*, **9**, 816.

the literature of the subject. On preparing the chloride for the above purpose, we analyzed the larger crystals and found that we had not a monochloride, but a dichloride.

Carbodiphenylimidedichloride, $C(NC_6H_5)_2.2HCl$.—6 grams freshly prepared carbodiphenylimide (B. p. 187°–8° at 20–22 mm., after two fractionations) was dissolved in 120 grams pure dry benzene. When pure, both the oil and its solution are entirely colorless. On passing dry hydrochloric acid into the solution (not cooling) it remains clear for the first few minutes. Then a voluminous precipitate suddenly appears, apparently almost entirely taking the place of the liquid. On continuing the current, and rotating the flask to aid in the solution of hydrochloric acid, the mixture gradually clears up, and finally, almost everything goes into solution. Sometimes a few distinct transparent crystals remain undissolved.

The whole is allowed to stand over night, care being taken to exclude moisture. In the morning a large quantity of the transparent crystals is found deposited. The liquid is poured off, the crystals brought rapidly on a Hirsch funnel, washed with benzene, and brought on a clay plate into a vacuum desiccator over sulphuric acid, potassium hydrate, and vaseline. After twenty-four hours, the crystals for analysis were finely powdered and again placed in the vacuum desiccator for a day.

Analysis.—

1. 0.2163 gram substance, heated with lime, required 16.0 cc. $\frac{N}{10}AgNO_3$ solution (Volhard).

2. 0.2223 gram substance, heated with lime, required 16.33 cc. $\frac{N}{10}AgNO_3$ solution (Volhard)

	Calculated for $(C_6H_5N)_2C.2HCl$.	Found.	
		1.	2.
Cl	26.59 per cent.	26.26	26.08

The compound is, therefore, carbodiphenylimidedichloride. The crystals are thick, short prisms with pyramidal terminations, apparently tetragonal or orthorhombic. The substance begins to decompose and melt at 130°, the action becoming violent at 145°. It is, therefore, impossible to speak of a constant melting-point. When heated, a yellow substance, probably one of the carbodiphenylimides, remains, and a gas,

found to be hydrochloric acid, is given off. The dichloride is quite soluble in hot chloroform and is reprecipitated unchanged by ligroin. It is quite stable when kept from moisture or organic matter. In contact with these it loses hydrochloric acid. A specimen, kept ten days in a corked tube, attacked the cork somewhat and, on analysis, gave:

1. 0.2172 gram substance, heated with lime, required 15 cc. $\frac{N}{10}AgNO_3$ solution (Volhard).

2. 0.3415 gram substance gave 0.3403 gram AgCl (Carius).

	Calculated for $(C_6H_5N)_2C_2HCl$.	Found. 1.	2.
Cl	26.59 per cent.	24.51	24.65

Boiled with water, or better, with aqueous alcohol, the dichloride gives carbanilide (M. p. 235°). In preparing the dichloride it is necessary to use, pure, freshly prepared liquid carbodiphenylimide. If solid carbodiphenylimide is present, hydrochloric acid colors the benzene solution yellow, and the crystals formed are more or less coated with a yellow sticky mass. The constitution of the dichloride has not been determined. It may be $(C_6H_5NH)_2CCl_2$ if the second molecule of hydrochloric acid adds in the same way as the first (see below), and it may be $ClC(NC_6H_5)(NHC_6H_5)HCl$, the chloride of chlorformdiphenylamidine. An attempt will be made to decide the question experimentally.

Carbodiphenylimidesesquichloride (?), $[(C_6H_5N)_2C]_3HCl$ or $(C_6H_5HN)_2CCl_2 + C_6H_5NHC(NC_6H_5)Cl$. — The voluminous precipitate first formed, (see page 108), on passing hydrochloric acid into carbodiphenylimide in benzene solution likewise contains more chlorine than the monochloride. As soon as the voluminous precipitate is formed, the current is stopped and the precipitate treated as above. The result is the same, whether the mixture is cooled or not. A white mass, of pearly luster, remains on the clay plates. For analysis, this was powdered, and again put in the vacuum-desiccator for twenty-four hours. Analyses of five different preparations were made:

1. 0.2283 gram substance, heated with lime, required 14.4 cc. $\frac{N}{10}AgNO_3$ solution (Volhard).

2. 0.2293 gram substance, heated with lime, required 14 cc. $\frac{N}{10}AgNO_3$ solution.

3. 0.3051 gram substance, heated with lime, required 17.9 cc. $\frac{N}{10}$ $AgNO_3$ solution.

4. 0.1805 gram substance, heated with lime, required 10.08 cc. $\frac{N}{10}$ $AgNO_3$ solution.

5. 0.2047 gram substance, heated with lime, required 13.08 cc. $\frac{N}{10}$ $AgNO_3$ solution.

Calculated for $(C_6H_4N)_2C.ClH$ = 15.4 per cent. Cl.
" " $[(C_6H_4N)_2C]_2HCl$ = 21.4 per cent. Cl.
" " $(C_6H_4N)_2C.2HCl$ = 26.59 per cent. Cl.

	1.	2.	3.	4.	5.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Found,	22.39	21.67	20.83	19.82	22.68

The substance may be a mixture of monochloride and dichloride in nearly molecular quantities. It was very frequently obtained and seems to have more or less characteristic properties by which it can be identified. It melts with decomposition at 115°–125°, the evolution of hydrochloric acid being strongest and completed at 150°. It is extremely soluble in cold chloroform and not insoluble in benzene.

Carbodiphenylimidemonochloride or Chlorformdiphenylamidine.[1]

$ClC(NHC_6H_4)(NC_6H_4)$.—Special precautions must be observed if only one molecule of hydrochloric acid is to be added to one molecule of di-imide. Weith says nothing regarding the details in the preparation of the monochloride which he analyzed[2] nor does he give any properties or physical constants by which it may be identified.

Only once in working as he did with a cold, concentrated benzene solution of the di-imide (5 grams in 3 or 4 volumes of benzene) did we obtain a compound whose analysis and behavior showed it to be, approximately, pure monochloride. As soon as a small quantity of precipitate was formed, the current of hydrochloric acid was stopped, the flask which had been kept in ice-water allowed to assume the temperature of the room, the precipitate washed with ligroin (B. p. 70°–80°), and

[1] The compound may be called carbanilide imidechloride, using Wallach's nomenclature (Ann. Chem. (Liebig), **184**, 4). It is a representative of the true urea-chlorides (carbamidechlorides) $NH_2C(NH)Cl$ as distinguished from the chlorformamides which are sometimes incorrectly so called.

[2] Ber. d. chem. Ges., **7**, 11.

treated as usual. The compound began to soften at 70° and had melted entirely at 110°. Analysis:

0.2644 gram substance required, when burned with lime, 11.83 cc. $\frac{N}{10}$ $AgNO_3$ solution (Volhard).

Calculated for $(C_6H_5N)_2CHCl$.	Found.
Cl 15.40	15.88

In a very large number of experiments, however, the precipitate formed by this method contained much more dichloride, and showed the properties of the mixture or sesquichloride described above. The pure monochloride was finally obtained as follows: 5 grams freshly-prepared di-imide was dissolved in 40–50 cc. ligroin (B. p. 40°–60°), cooled in ice-water and hydrochloric acid led into the solution. A precipitate was at once formed, and, after a few moments, and before the precipitation was complete, the deposit was rapidly brought on a filter, washed with ligroin, and dried as usual. Analysis:

0.366 gram substance heated with lime, required 15.65 cc. $\frac{N}{10}$ $AgNO_3$ solution (Volhard.)

Calculated for $(C_6H_5N)_2CHCl$.	Found.
Cl 15.40	15.18

Chlorformdiphenylamidine (carbodiphenylimidechloride) melts completely at 92°–95° with slight evolution of gas, this increasing on raising the temperature. It is readily soluble in chloroform and benzene, and reprecipitated by ligroin. The presence of dichloride raises its melting-point. On treating the filtrate from the chlorformdiphenylamidine with more hydrochloric acid a heavy precipitate was formed. Analysis showed this to be a mixture of di- and monochloride. Even when only the calculated quantity (1 molecule) of hydrochloric acid (a measured volume of the gas or its ethereal solution) was added to a ligroin solution of the di-imide (1 molecule), the precipitate was a mixture of the two chlorides (containing 16.6 per cent. Cl instead of 15.4 per cent. as in monochloride), while the filtrate contained unchanged di-imide. In preparing pure chlorformdiphenylamidine the yield is small, as much less than the calculated amount of hydrochloric acid must be used. Carbodiphenylimidechloride gives, with sodium ethylate in the cold, ethyl-

isodiphenylurea, which makes it very probable that addition of hydrochloric acid to carbodiphenylimide takes place according to the equation

$$C_6H_5N:C:NC_6H_5 + HCl = C_6H_5N:C<^{Cl}_{NHC_6H_5},$$

forming chlorformdiphenylamidine and not a simple salt of carbodiphenylimide, $C(NC_6H_5)(NC_6H_5HCl)$.

Action of Sodium Ethylate on Chlorformdiphenylamidine. Ethoxyformdiphenylamidine or Ethylisocarbanilide, $C_6H_5OC(NHC_6H_5)(NC_6H_5)$.

Six grams (1 molecule) chlorformdiphenylamidine was added in portions to a cold solution of sodium ethylate (0.6 gram sodium, 1 atom) in 15 grams absolute alcohol. After ten minutes it was poured into about a liter of cold water, extracted with ether, the ethereal solution washed 5 or 6 times with a little water, filtered, and dried for eighteen hours over anhydrous sodium sulphate. On distilling off the ether, an oil and a few crystals, identified as carbanilide, remained. The oil could be separated from the carbanilide by dissolving in ligroin. After removing the ligroin, the oil was distilled in a vacuum. The main fraction came over at 205°–206° at 25 mm., and showed all the other properties of ethoxyformdiphenylamidine. It remains a mobile oil even after standing for some time, while carbodiphenylimide becomes thick and then solid. With dry hydrochloric acid, at 100°, it gave[1] ethyl chloride, burning with green-tinged flame, and carbanilide, melting at 235°, $(C_6H_5N)(C_6H_5NH)COC_2H_5 + HCl = (C_6H_5NH)_2CO + C_2H_5Cl$. The formation of the compound takes place according to the equation:

$$(C_6H_5N)(C_6H_5NH)CCl + NaOC_2H_5 = (C_6H_5N)(C_6H_5NH)COC_2H_5 + NaCl.$$

This reaction may be used to prepare the isoureaethers, the use of sealed tubes being thus avoided.

It is not necessary to isolate the chlorformdiphenylamidine, the best yield being obtained as follows:

Ten grams freshly prepared carbodiphenylimide is dissolved in 30 to 40 cc. absolute alcohol, the solution cooled in ice-

[1] Ber. d. chem. Ges., **27**, 927.

water, the calculated amount of ethereal hydrochloric acid (we used 9.5 cc. of a 20-per cent. solution) added, and the mixture poured into a cooled solution of sodium ethylate (1.2 grams sodium). After a few minutes the mixture is poured into cold water and treated as above. A good yield (7.5 grams) of ethylisocarbanilide was obtained as a colorless, mobile oil, which boiled at 205°–207° at 25 to 26 mm.

This work shows that when hydrochloric acid is taken up by acid derivatives, $XC<^{NC_6H_5}_{OR}$ or $Y''=C=NC_6H_5$ containing the phenylimide group, a double bond is opened and the group $C<^{NHC_6H_5}_{Cl}$ formed. Further work in this direction is being done.

ON SOME BROMINE DERIVATIVES OF PARAISOBUTYL PHENOL.

By F. B. Dains and I. R. Rothrock.

Monobromparaisobutyl Phenol.—When the dry sodium salt of *p*-isobutyl phenol is suspended in dry carbon bisulphide and bromine (1 molecule) added, the solution is soon decolorized with the separation of sodium bromide. After filtering and distilling off the carbon bisulphide a dark-colored oil is left. This is best purified by distilling with steam, which carries over a colorless aromatic oil, which, in turn, soon solidifies. The solid product may be dried on a clay plate and crystallized from low-boiling petroleum. From this solvent monobrom *p*-isobutyl phenol separates out in fan-like clusters of blunt needles, which melt at 50°. It is very easily soluble in ordinary organic solvents. Analysis:

0.2634 gram substance gave 0.2150 gram AgBr.

Found.	Calculated for $C_{10}H_{13}OBr$.
Br 34.73	34.93 per cent.

The same product can be obtained by treating the free *p*-isobutyl phenol dissolved in water or carbon bisulphide with the calculated amount of bromine.

The benzoyl ether of monobromparaisobutyl phenol was obtained by dissolving the phenol in caustic soda and adding the proper amount of benzoyl chloride. The solid formed was purified by crystallization from methyl alcohol and low-

boiling petroleum. The fine needle-like crystals melt at 78.5°. Analysis:

0.2430 gram substance gave 0.1373 gram AgBr.

Found.	Calculated for $C_4H_9.Br.C_4H_3.OCOC_6H_5$.
Br 24.04	24.02 per cent.

Dibromparaisobutyl Phenol.—When *p*-isobutyl phenol (1 molecule) is treated with bromine (2 molecules) in water, carbon bisulphide, or acetic acid solution, there is formed the dibrom substitution-product. It is best purified by crystallization from ligroin, from which it separates out in large yellowish plates melting at 78°. These crystals are often very large. One of them was 30 mm. long, 22 mm. wide, and 6 mm. thick. The substance dissolves easily in organic solvents. Analysis:

0.1590 gram substance gave 0.1946 AgBr.

Found.	Calculated for $C_4H_9.Br_2.OH.C_4H_2$.
Br 52.08	51.94 per cent.

When the phenol is treated in solution with an excess of bromine (3 or 4 molecules) the only definite product formed seems to be the dibromparaisobutyl phenol. Efforts were made to determine the position of the bromine atoms by oxidizing the isobutyl group to carboxyl, thus forming a derivative of *p*-hydroxybenzoic acid. Potassium bichromate and sulphuric acid, potassium permanganate in alkaline solution, and chromic acid in acetic acid solution, were found to break up the molecule completely, giving no benzoic acid.

It is exceedingly probable, however, from analogous reactions, that the bromine atoms are both ortho to the hydroxyl—thus giving an orthobromparaisobutyl phenol and a diorthobromparaisobutyl phenol.

ON THE ACTION OF ACID CHLORIDES ON THE METHYL ETHER OF PARAISOBUTYL PHENOL.

By F. B. Dains.

It has been shown by Gattermann[1] and others that phenol ethers react with acid chlorides in the presence of aluminum chloride, forming substituted ketones.

[1] Ber. d. Chem. Ges., **22**, 1129; **23**, 1199.

With a simple phenol ether, or with an ortho[1] or meta[2] substituted phenol ether, the entering radicle goes in the para position. It was thought to be of interest to investigate the action of acid chlorides upon para-substituted-phenol ethers.

This preliminary report is now published, since further work along this line must be deferred for a short time.

Ortho-methoxymetaisobutyl Acetophenone.

One part of the methyl ether of *p*-isobutyl phenol and one part acetyl chloride are dissolved in carbon bisulphide or, better, ligroin [B. p. 70°–80°] in a flask fitted with a reflux condenser, and two parts aluminum chloride slowly added. The reaction begins at once with evolution of hydrochloric acid. To complete the reaction the flask is heated on the water-bath. After cooling, the excess of solvent is poured off, and the black residue in the bottom of the flask is decomposed with water. The oil that separates out is taken up with ether, dried, and distilled. The bulk of the oil passes over between 262° and 265°, at 749 mm. When freshly distilled it is of a light yellow color, but soon assumes a greenish tinge. Analysis:

I. 0.2757 gram substance gave 0.7644 gram CO_2 and 0.2096 gram H_2O.

II. 0.2304 gram substance gave 0.6395 gram CO_2 and 0.1805 gram H_2O.

	Found.		Calculated for $C_6H_3\begin{cases}OCH_3\\C_4H_9\\COCH_3\end{cases}$
	I.	II.	
C	75.62	75.69	75.73
H	8.44	8.71	8.74

Orthomethoxymetaisobutyl acetophenone does not solidify at −18°.

When this ketone is dissolved in alcohol, the proper amount of hydroxylamine hydrochloride and sodium carbonate added and the mixture allowed to stand, the corresponding ketoxime is formed. This was purified by dissolving in caustic soda. From the oil obtained, crystals separate out on standing in a desiccator. These dried on a clay plate and crystallized from ligroin form needles melting at 113°–114°. Analysis:

[1] Ann. Chem. (Liebig), **244**, 64. [2] Ber. d. chem. Ges., **21**, 2270.

0.2208 gram substance gave 13.7 cc. N at 27° and 747 mm.

	Found.	Calculated for $C_{13}H_{19}NO_3$.
N	6.78	6.34 per cent.

The Action of Benzoyl Chloride.

Orthomethoxyparaisobutyl Benzophenone.

8 grams of methyl ether and 7 grams of benzoyl chloride were dissolved in carbon bisulphide and 12 grams aluminum chloride added slowly. The dark-colored product of the reaction was decomposed with water, the oil taken up with ether, dried, and distilled. Above 315° there came over a light-colored oil which changed to a greenish color on standing. Analysis:

0.2768 gram oil gave 0.1863 gram H_2O and 0.8141 gram CO_2.

	Found.	Calculated for $C_{18}H_{20}O_2$.
C	80.28	80.60
H	7.48	7.46

There is not much doubt that the entering acyl group is in the ortho position to the methoxy group. Gattermann has found, for instance, that *p*-cresolmethyl ether and urea hydrochloride under like conditions form orthomethoxymetatoluic acid amide.[1] This point will be proved experimentally later, and the action of acid chlorides on other para-substituted-phenol ethers and on mesitylol investigated.

THE EFFECT OF HYDROLYSIS UPON REACTION-VELOCITIES.[2]

By F. L. Kortright.

In almost all of the cases where reaction-velocities in aqueous solution have been studied according to the "Mass Law" of Guldberg and Waage, the reactions have been between substances which are practically non-hydrolyzed and in these cases the amount of each substance actually taken for the experiment can be considered the *active mass*. When, how-

[1] Ann. Chem. (Liebig), **244**, 66.

[2] In this article the term "hydrolysis" is employed instead of the more cumbersome term "hydrolytic dissociation," to indicate the decomposition of a salt in aqueous solution, into a base and an acid by the action of the water. The salt so decomposed is "hydrolyzed."

ever, one or more of the substances taking part in the reaction is hydrolyzed, the total amount of the substance used can not be taken as its *active mass;* only the non-hydrolyzed portion can be so considered. A case of this kind has recently been given by Kahlenberg[1] in an excellent experimental paper on the velocity of the reaction between ferric chloride and stannous chloride. Unfortunately, he has, however, calculated his results on the assumption that the *active mass* of the reacting substances is the total amount taken, while in reality, since ferric chloride and stannous chloride are strongly hydrolyzed, the *active mass* is much less. That this is true may be seen from the following considerations:

The generally accepted expression for the reaction-velocity in a bimolecular reaction, where the two substances are taken in equimolecular amounts, and the reaction goes as good as completely in one direction, is

$$dx/dt = c(a-x)^2 \qquad (1)$$

where a represents the amount of substance present at the beginning, x the amount of substance which has been transformed during the time t, and c is the proportionality-factor. Integrating from 0 to t and noting that for $t=0$, $x=0$, there results

$$x/t(a-x) = ac = \text{const.} \qquad (2)$$

If the reaction takes place according to the equation

$$Fe_2Cl_6 + SnCl_2 = Fe_2Cl_4 + SnCl_4,$$

that is if the reaction takes place between the total amount of ferric chloride and stannous chloride present, then equation (2) should hold good and its left member should, at constant temperature, maintain a constant value. When the experimental data are substituted in equation (2) it gives, in the experiment where the conditions for hydrolysis are best, a value for $x/t(a-x)$ varying from 0.00921 to 0.00536 in 140 minutes and falling to 0.00421 at the end of 320 minutes, with a constant decrease from the upper to the lower value and, where the conditions for hydrolysis are poorest, a value varying from 0.0721 to 0.0468 in 130 minutes. In some experiments two or three consecutive values of the constant lie

[1] J. Am. Chem. Soc., **16**, 314.

closely together, but in these cases a plat of the curve expressing $x = \varphi(t)$ shows that these values fall off from the curve and are due to experimental error. This result must lead to the conclusion that either something is wrong with the experimental work or with the formula. The experimental values of $x = \varphi(t)$ form as smooth a curve as might be expected and, therefore, the trouble must be in the formula.

When ferric chloride is dissolved in water a reaction takes place between the water and the salt, in which the chlorine of a portion of the ferric chloride is replaced by the hydroxyl of the water, and hydrochloric acid is set free according to the equation

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl,$$

in which the ferric hydroxide is a soluble colloidal form which may be considered electrolytically undissociated. The remainder of the ferric chloride is almost entirely dissociated electrolytically into ferric and chlorine ions. In the same way there is a reaction between the water and the stannous chloride with the formation of basic tin chloride according to the equation

$$SnCl_2 + H_2O = SnCl(OH) + HCl,$[1]$$

and the remainder is electrolytically dissociated into stannous and chlorine ions. Therefore in the solution at the beginning there are undissociated colloidal ferric hydroxide, basic tin chloride, a *small* amount of the undissociated salts, and ferric, stannous, chlorine, and hydrogen ions. Since, as is well known, all inorganic chemical reactions in aqueous solution seem to take place between the ions of the reacting substances, it is safe to conclude that here the reaction is not between the total amount of salts in solution, but merely between that amount of each which is present as ions. Upon this assumption the reaction may be written

$$2Fe^{+++} + 6\overline{Cl} + Sn^{++} + 2\overline{Cl} = 2Fe^{++} + 4\overline{Cl} + Sn^{++++} + 4\overline{Cl}$$

or, since the $\overline{Cl}$ is the same on each side, we may write

$$2Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++}$$

[1] Kahlenberg found this hydrolysis to take place to such an extent that he was obliged to partially repress it by the addition of hydrochloric acid in order to keep his solution clear.

where the + and — marks have the significance usually assigned to them in reactions of this kind.

If the assumption that the reaction consists of a transfer of electrical charges from the ferric to the stannous ions, be correct, it is necessary to determine the concentration of these ions at the time t, in order to apply the "Mass Law" to a study of the velocity of the change.

The amount of undissociated salt is so small that it is possible to consider all except the hydrolyzed portion in the form of ions, and the problem resolves itself into finding an expression which will give a as a function of the hydrolysis at the time t.

Since tin and iron are nearly equally strong bases we may assume that they are equally effected by the water and since the experiments were carried out using equimolecular amounts of each salt, we may assume that the relation continues equimolecular, and by platting $x=\varphi(t)$ we can select a point where the curve becomes nearly parallel to the t axis and $(a-x)=h$ is approximately the amount of hydrolyzed substance at that time. Assuming that the hydrolysis is constant throughout the time of the experiment, (which is sufficiently correct for our purpose) the active mass at the beginning of the experiment becomes $(a-h)=a'$. By substituting this value for the initial *active mass* in equation (2), it gives

$$x/t(a'-x)=a'c=\text{const.} \qquad (3)$$

In the following tables t is the time in minutes, x the amount of substance which has been transformed during the time t, ac is the value of $x/t(a-x)$ obtained from equation (2) and $a'c$ is the value of $x/t(a'-x)$ obtained from equation (3). Varying amounts of hydrochloric acid were added to the solutions in the experiments and this is indicated at the head of each table.

A description of the experimental method used in obtaining these results may be found in the article by Kahlenberg.[1]

[1] *Loc. cit.*

I.

(25 cc. Hydrochloric Acid Added.)

t	x	ac	$a'c$
0	....	.....	.....
10	2.20	0.0721	0.0804
20	3.10	0.0721	0.0844
25	3.35	0.0705	0.0845
35	3.70	0.0682	0.0856
50	3.95	0.0608	0.0802
70	4.20	0.0571	0.0816
100	4.40	0.0518	0.0822
130	4.50	0.0468	0.0796

$a = 5.25$ $a' = 4.935$

II.

(20 cc. Hydrochloric Acid Added.)

t	x	ac	$a'c$
0	....	.....	.....
10	1.60	0.0508	0.0521
21	2.40	0.0486	0.0544
50	3.25	0.0433	0.0520
70	3.55	0.0423	0.0534
95	3.80	0.0421	0.0571

$a = 4.75$ $a' = 4.50$

III.

(15 cc. Hydrochloric Acid Added.)

t	x	ac	$a'c$
0	....	.....	.....
10	1.40	0.0368	0.0426
20	2.15	0.0352	0.0424
30	2.60	0.0333	0.0416
40	2.95	0.0328	0.0426
50	3.25	0.0333	0.0454
70	3.50	0.0292	0.0423
80	3.65	0.0294	0.0442
90	3.75	0.0287	0.0448

$a = 5.2$ $a' = 4.68$

IV.

(10 cc. Hydrochloric Acid Added.)

t	*x*	*ac*	*a'c*
0	....	.....	.....
10	1.55	0.0298	0.0369
20	2.40	0.0276	0.0359
30	2.95	0.0259	0.0352
40	3.40	0.0254	0.0363
50	3.65	0.0236	0.0349
70	4.10	0.0216	0.0357
100	4.40	0.0187	0.0328
120	4.60	0.0178	0.0336
150	4.90	0.0177	0.0388

$a = 6.75$ $a' = 5.74$

V.

(5 cc. Hydrochloric Acid Added.)

t	*x*	*ac*	*a'c*
0	....	.....	.....
10	1.50	0.01911	0.0259
35	3.60	0.01789	0.0278
50	4.15	0.01596	0.0264
70	4.65	0.01413	0.0252
80	5.00	0.01437	0.0273
110	5.55	0.01327	0.0284
140	6.00	0.01279	.....
170	6.35	0.01245	.....

$a = 9.35$ $a' = 7.29$

VI.

(No Hydrochloric Acid Added.)

t	*x*	*ac*	*a'c*
0	....	.....	.....
10	0.93	0.00921	0.0172
20	1.58	0.00836	0.0166
40	2.43	0.00706	0.0156
60	2.93	0.00603	0.0144
80	3.43	0.00564	0.0147
100	3.96	0.00560	0.0167
120	4.33	0.00539	0.0183
140	4.73	0.00536	.....
190	5.23	0.00475	.....
250	6.00	0.00477	.....
320	6.33	0.00421	.....

$a = 11.03$ $a' = 6.33$

The above tables show that $a'c$ calculated by this means is much more nearly constant than ac, and that the variation between the values of $a'c$ is such as would be produced by experimental error. In the first four tables $a'c$ is calculated for all of the experimental values and is as nearly constant as can be expected with the exception of the last value in each table, where the experimental determination is subject to a large error. In the tables V and VI $a'c$ is not calculated for the final values, for in these cases the hydrolysis has been but slightly depressed by the addition of hydrochloric acid, and therefore the assumption that it is constant throughout the reaction, leads to a greater error than in the cases where the hydrolysis is not so great in amount. In these two cases, however, a fairly good constant can be calculated for the most important range of the tables.

A comparison of the values of ac and $a'c$ in the six tables shows conclusively that the hydrolysis has a very important, and calculable, effect on the constant. The fact that the error in ac continuously increases with the diminishing concentration of the hydrochloric acid leads to the same conclusion.

CORNELL UNIVERSITY,
December, 1894.

ON THE INFLUENCE OF MAGNETISM ON CHEMICAL ACTION.[1]

BY F. A. WOLFF, JR.

Although the influence of magnetism on chemical action has been the subject of numerous investigations, the conclusions drawn by the various experimenters who have dealt with this problem are in many instances contradictory.

In the following brief résumé, the earlier investigations may be passed over, as they really did not bring to light any positive evidence one way or the other. In some cases a repetition of the experiments has even failed to verify the results recorded. Those made by Robert Hunt belong to this class, as Prof. Remsen has been unable to reproduce any of Hunt's results.

[1] From the author's thesis, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, June, 1893.

In 1881 Prof. Remsen[1] discovered the remarkable influence exerted by a magnet on the deposition of copper, from one of its solutions, on an iron plate. In Prof. Remsen's own words: "When copper is deposited from a solution of copper sulphate on a plate of iron placed on the poles of a magnet, it is arranged in ridges around the poles in directions which are at right angles to the lines of force and consequently coincident with the lines marking the equipotential surfaces. Furthermore, the outlines of the poles of the magnet are always sharply defined on the plate as along these lines a portion of the iron of greater or less width is left unacted upon." The appearance of the plate is shown in Fig. 1.

This experiment redirected attention to the subject and Messrs. Nichols and Franklin[2] were the next to conduct experiments in this field.

They found that "passive" iron loses its passivity when brought into a magnetic field; also that when two iron electrodes, only one of which is magnetized, are dipped into a solution capable of acting upon them chemically, an electric current is established in the solution from the magnetized to the unmagnetized electrode.

Prof. Rowland and Bell[3] were the first to observe the opposite effect. Experiments were made by them with iron, cobalt, and nickel electrodes in 30 different electrolytes; the electrodes were of different shapes, one sharply pointed and the other blunt, so that, when placed in a uniform magnetic field, they would become unequally magnetized. In all the cases examined they detected the existence of a current from the less strongly to the more strongly magnetized electrode, indicating that the latter was being protected. As Prof. Rowland has pointed out, the protection should be greatest where the rate of variation of the square of the magnetic force is a maximum.

Somewhat similar experiments were made by Andrews[4] and Gross,[5] who, however, obtained results analogous to those of Nichols and Franklin.

Loeb[6] has approached the subject from a different direction, by determining the rate of oxidation of a ferrous salt and

[1] This Journal, **3**, 157; Science, **1**, 36. [2] Am. J. Sci., **31**, 272; **34**, 419; **35**, 290.
[3] Phil. Mag., **26**, 105.
[4] Proc. Roy. Soc., **44**, 152; **46**, 176. [5] Sitzungsber. d. Wien. Akad., **112**, 1373.
[6] This Journal, **13**, 145.

also the rate of reduction of a ferric salt, both within and outside of a magnetic field. No effect was detected in either case.

Lately, Andrews[1] has published another contribution to this subject, in which he shows that the rate of deposition of copper on iron bars, placed in a solution of copper sulphate, is accelerated by magnetizing them.

Last year in this laboratory, Mr. Geo. O. Squier[2] resumed the investigations of Rowland and Bell. His principal conclusions may be summarized as follows:

1st. When a pointed and a plane electrode of iron are placed between the poles of an electro-magnet in a solution capable of chemically acting on them, on first making the field, a current of small magnitude is always observed in such a direction as to indicate that the point is being protected from the action of the reagent.

2nd. That this current is momentary and is soon reversed in direction, if aqueous solutions be employed, and can often only be detected when bodily motion of the reagent is prevented by decreasing its fluidity with gelatin or some similar substance.

3rd. That this reversal is due to the concentration of the iron salts formed in the reaction, around the more strongly magnetized parts of the electrodes, and is *not* due to any *direct* influence exerted by the magnet.

Thus the directly opposite results obtained by Rowland and Bell were reconciled with those of Nichols and Franklin, Andrews, and Gross.

While this work was still in progress Mr. Squier and the writer undertook a joint investigation of the subject, under the direction of Prof. Rowland, to whom they are indebted for many valuable suggestions, from the point of view of Prof. Remsen's experiments. This seemed all the more promising since the "protective" effect as detected by the galvanometer was so very small, while in these experiments the effect was so very striking. The first part of this paper is therefore a joint production, but the writer was forced to pursue the investigation alone, owing to Mr. Squier's inability to continue the work in consequence of his professional duties.

[1] Proc. Roy. Soc., **32**, 114. [2] Phil. Mag., **35**, 473.

The Rotations in the Liquid.

The original experiments of Prof. Remsen were first carefully repeated. Next to the absence of deposit over the outlines of the pole and the deposition in ridges, the phenomena which are most striking when a solution of copper sulphate is poured on an iron plate placed in a magnetic field, are the rotations in the liquid. In the course of a large number of experiments, using pole-pieces and plates of various forms, it was soon found that the rotations in the solution were connected with variations in the degree of magnetization of the plates and could, therefore, be made as complicated as possible by simply varying the form of the pole-piece. In one experiment the positions of minute iron screws, connecting the parts of the electro-magnet used, were indicated by rapid rotation of the liquid on the plate immediately above. In general, iron placed beneath the plate in any position produced local rotations in the liquid above.

That these rotations are electro-magnetic is quite evident. As was shown by Squier, when iron is attacked in a magnetic field, electric currents are established from the less strongly to the more strongly magnetized parts. This effect, being quite minute, is soon overpowered by secondary effects (the accumulation of the iron salts in the strongest parts of the field) which gives rise to currents in the opposite direction, and to these the rotations seem principally to be due. If the iron is not completely covered by a copper-deposit, local voltaic currents must also exist, and these, on account of the non-uniformity of the field, would, by its action, produce a resultant motion of the liquid. It would be quite difficult to take into account all of the effects when, besides, the viscosity of the solution introduces additional complication.

The simplest rotations observed were obtained when a pointed pole-piece was used. With circular plates there was only one rotation which was uniformly dextro above a north pole and levo above a south pole. These may be explained by the action of the field on the current from the part immediately above the pole-piece to adjoining parts of the plate.

With cylindrical pole-pieces the effects are more complicated as three distinct rotations may be observed. Above a north pole

the phenomena are as follows: The outlines of the pole are clearly marked by the absence of deposit. Inside this ring the rotation is dextro, and the deposit comparatively uniform. Directly over the ring and for some distance beyond, the rotation is levo and quite rapid. With larger plates a third rotation, dextro, of smaller angular velocity than the one over the outlines of the pole is seen. Whether this third rotation depends on *local* voltaic currents has not been determined.

That the main rotations are due to the concentration effects is shown by introducing with a pipette a few drops of a solution of ferric chloride above the center of a plate covered with water and placed on the pole of a magnet. The outlines of a pole are marked by a yellow ring due to the solution of ferric chloride which has been drawn up to it and the rotations begin immediately.

On pouring over the plate, dilute nitric acid, containing in solution the lower oxides of nitrogen, instead of copper sulphate, the outlines of the pole appear almost immediately as a dark ring due to the interaction of the ferrous salt formed in the reaction and the oxides of nitrogen.

Distribution of the Deposit.

It has been suggested that the absence of deposit over the outlines of the pole and the deposition in ridges is *directly* due to the magnetized condition of the metal. Let us, however, inquire how far the distribution of the deposit *could* be the result of the currents in the liquid and the concentration of the iron salts formed during the reaction, in the strongest parts of the field.

1st. Over the outlines of the pole there is no deposit.

The continual accumulation of iron salts in this region would certainly tend to decrease the amount of copper deposited there, and, moreover, the currents which originate there and proceed outward and inward *from* the "protected region" to other parts of the plate are accompanied by a corresponding amount of electrolysis. A certain quantity of iron goes into solution there, just as in other parts of the plate, but the equivalent amount of copper is deposited elsewhere on the plate, in excess of the amount being deposited on those parts by the normal action of the copper sulphate on the iron. These cur-

rents, since they go in the solution *from* the "protected region" to the other parts of the plate, should entirely prevent the deposition of copper over the outlines of the pole as the combination really constitutes a two-fluid cell, iron in contact with a solution of iron salts, and iron in contact with a solution of copper sulphate.

2nd. Directly outside the outlines of the pole the deposit is greatest.

This would, likewise, be a result of the electrolysis accompanying the currents from the "protected region" since the electromotive force between the ridge and the outer regions of the plate is practically constant, and since the magnetization at the ridge is immensely greater than that of the outer portions of the plate, the current to any particular portion, and, therefore, the accompanying electrolysis, is inversely proportional to the distance of that portion from the protected ridge, (that is, to the resistance). Hence, the deposit is thickest immediately adjoining the "protected ridge" marking the outlines of the pole. The deposit on the inside of the "protected region" also shows some indication of this action, but to a very much smaller degree, as one might expect since the degree of magnetization of these parts is more comparable with that over the outlines of the pole.

It is, therefore, quite probable that the absence of deposit over the outlines of the pole is not due to any *direct* influence of magnetism on chemical action, as has heretofore been supposed.

The question that still remained was, why is the deposit broken up in ridges?

On the Deposition in Ridges.

A number of possible explanations of this curious phenomenon suggest themselves.

1st. That the deposition in ridges is *directly* due to the magnetized condition of the iron.

2nd. That it is due to the presence of the voltaic currents, to which the absence of deposit over the outlines of the pole has been attributed.

3d. That it is produced by the mechanical flow of the solution over the plate.

A number of reasons point to the improbability of the first

hypothesis, as will be pointed out later. The second hypothesis was therefore the first to be tested.

Voltaic Currents.

Since the existence of an electric current arising from concentration of the iron salts formed during the reaction about the outlines of the pole accounted so well for the absence of deposit and the gradation of the deposit, it was thought that the deposition in ridges might also, in some way, be connected with it. Accordingly, an attempt was made to produce ridges by means of an extraneous current, within the region in which the deposit is practically uniform.

A pointed zinc rod was brought in contact with the center of an iron plate on the pole of a magnet and a solution of copper sulphate poured on as before. On examination, the deposit within the outlines of the pole was found to be arranged in spirals radiating from the point where the zinc rod touched the plate. Over a north pole the spirals were turned to the left, and on reversing the current in the electromagnet the spirals were turned in the opposite direction.

This curious phenomenon was all the more perplexing since it seemed to indicate that magnetism, at least in this special case, is *not* the direct cause of the deposition in ridges.

Prof. Rowland[1] has pointed out that, in consequence of the "Hall effect" the lines of flow of a current proceeding to or from a center in a thin metallic plate, placed in a magnetic field at right angles to the lines of force, would become spirals instead of radii. If, therefore, copper *should* be deposited in ridges along the lines of flow of a current in an iron plate on which is poured a solution of copper sulphate, this would furnish a possible explanation of the deposition in spirals. This supposition was accordingly tested. Since the "Hall effect" is opposite, in the case of nickel and iron, the spiral ridges, if formed, should from this cause turn in opposite direction when iron is replaced by nickel. It was found that mercury and platinum when deposited from their solutions on nickel, in a magnetic field, are not deposited in ridges, although the outlines of the pole are marked by the absence of deposit. Experiments along these lines gave, consequently, no definite results.

[1] Phil. Mag., 10, 301.

Experiments were next made on the deposition of copper on iron plates through which currents were flowing, both inside and outside the magnetic field. In the latter case it was found that the presence of a current did not destroy the uniformity of deposit until the strength of the current was sufficient to magnetize the plate to an appreciable extent. With a current of 150 amperes the copper was deposited in ridges along the lines of flow of the current. Small currents in an iron plate placed in a magnetic field did not seem to affect the form of deposit in the least, except when, as in the case of the zinc rod, a uniform motion in the solution was produced. This will be referred to below.

From these experiments the conclusion may be drawn that the deposition in ridges is not *directly* due to the voltaic currents existing in the solution or in the plate.

Bodily Motion of the Liquid.

That there is any effect due to the bodily motion of the liquid over the plate seemed at first improbable, for within the outlines of the pole where there is considerable rotation the deposit is uniform, and, moreover, when the plate is divided by a partition through the center, the ridges in either compartment do not seem to be in the least affected by it, as they begin immediately at the partition.

When a solution of nitric acid (15 per cent.) is used instead of copper sulphate, the outlines of the pole are soon marked by a dark ring and apparently before the liquid is set in bodily motion, dark markings, similar in appearance to the ridges of copper, are seen all over the plate. On pouring off the nitric acid the plate is found to be differently eaten away in different parts. The whole surface outside the protected ring is seen covered with circular markings, just as when copper is deposited on iron under the same circumstances.

To determine whether strains in the iron, which *do* exist in plates not uniformly magnetized, would produce any deposition in ridges when subjected to the action of copper sulphate, oblong rectangular strips of the metal were bent into circular arcs, and immersed in a solution of copper sulphate. It was found that the copper was uniformly deposited on them if they were carefully lowered into the solution. If,

however, they were rapidly plunged into the liquid, *the copper was deposited in ridges along the lines of first flow of the solution across the plate.*

When the strips were plunged into the solution with their concave side downward and inclined to the horizontal, the ridge on the concave surface converged toward the part of the strip which was last to be covered by the solution. See Fig. 2.

Similar effects were obtained when the convex side was held downward, the ridges being in the direction of first flow. Even with the non-magnetic metals, zinc and tin, the same result was obtained.

Fig. 3 shows the appearance of the under side of an iron plate, immersed in an inclined position in a solution of copper sulphate. It will be seen that the copper has been deposited practically in parallel ridges, along which the solution of the iron salt formed under these conditions would rise. The yellow solution was actually observed to rise from the upper edge of the plate in narrow columns corresponding to these ridges.

In the next experiments a steady stream of a solution of copper sulphate was caused to flow over metal plates from a small orifice. The deposit was in ridges along the lines of flow of the solution, and the same effects were obtained when iron, zinc, and tin were used. Fig. 4 illustrates its action on a tin plate under these circumstances.

These experiments show that ridges can be formed without the aid of magnetism by a mere mechanical flow, although it is not self-evident what the true explanation of this phenomenon is. That it is *not* due to any surface impurities of the solution was shown by first covering the plate with water and then allowing the solution to flow in beneath the surface of the water. As in the other cases, the copper was deposited in ridges along the lines of the flow. The spiral ridges obtained with the zinc rod were now readily accounted for, as, on closer inspection, solid particles suspended in the liquid were found to move spirally inward toward the point where the zinc rod and the iron plate were in contact.

* *Direct Effect of Magnetism.*

There are quite a number of reasons which speak against the supposition that the deposition in ridges is due to the direct effect of magnetism on chemical action:

1st. There can hardly be any discontinuity of the magnetization of an iron plate corresponding to the ridges formed when a solution of copper sulphate is poured over it.

2nd. Inside the protected region the deposit is uniform, while in this region ridges are easily produced by mechanical flow.

3rd. It has been suggested that wherever the action of the solution begins, a cavity is formed and that the adjoining parts (edges) would therefore be more strongly magnetized and hence, "protected" from the further reaction of the reagent.

But to explain the deposition in circular ridges, for example, when cylindrical pole pieces are used, it would be necessary to assume that the plate is first attacked by the reagent in circles.

4th. The initial irregularities of the plate would also be magnified if this were the controlling cause, and moreover, these are greater than any which might be produced in a short time by the action of the solution.

A number of experiments seem to indicate that the deposition in ridges in a magnetic field is due to the rotations produced by the interaction of the field and the electric currents existing in the solution, for when the conditions are so modified as to prevent any motion of the liquid in contact with the metal the ridges do not appear. This was done in the following two ways:

1st. Enough gelatin was added to a solution of copper sulphate to make it stiffen on cooling. When the warm solution was poured on an iron plate in a magnetic field no deposition in ridges could be observed.

The "protective" action as shown by the galvanometer, is, however, best exhibited under these circumstances.

2nd. Placing a piece of filter paper on an iron plate in a magnetic field and pouring over it a solution of copper sulphate produced a similar effect. Where the paper touched the metal no deposition of ridges was observed, but wherever it was wrinkled and not in contact with the plate, the ridges were quite marked.

If the true explanation of the ridges is mechanical, it ought to be possible to detect motion along the ridges and, unfortunately, this cannot always be done. When drops of a solution of copper sulphate are placed on an iron plate in a magnetic

field, the copper is deposited in ridges in the same direction as if the whole plate had been covered with the solution. At first there is considerable commotion in the drop but soon no motion can be detected with a magnifying glass. Therefore, if the deposition in ridges is mechanical, the lines of first flow of the solution in contact with the plate must be in the direction of the ridges afterwards formed. How such a motion could be set up is not quite clear, but that the prevention of motion is attended by an absence of ridges seems to show that they are causally related.

When copper is deposited on tin in a magnetic field a whirl is set up about the point where the deposition begins, and ridges begin to appear along the lines of flow of the liquid. As the action of the solution soon starts up in other parts of the plate these whirls interact and, as a result, the copper is deposited in ridges of the most varied patterns.

Whether the regular deposition in ridges in the case of iron is due to the fact that more points are simultaneously attacked by the solution and that these whirls produce a resultant motion in the direction in which the ridges afterwards appear, cannot be affirmed.

Conclusions.

The conclusions reached may be summarized as follows:

1st. That the *absence* of deposit over the outlines of the pole is *not* due to any *direct* influence of magnetism on chemical action.

2nd. That it is due to the accumulation of the iron salts formed in the reaction about those parts *and* to the electric currents therefrom arising.

3rd. The fact that the deposit is thickest immediately adjoining the protected region also finds its explanation in the electrolysis accompanying these currents.

4th. That the deposition in ridges is not due to any direct influence of magnetism on chemical action.

5th. That the deposition in ridges is not directly due to the voltaic currents in the liquid.

6th. That copper is deposited in ridges on both magnetic and non-magnetic metal when a solution of copper sulphate is allowed to flow over them and that the ridges are arranged along the lines of flow.

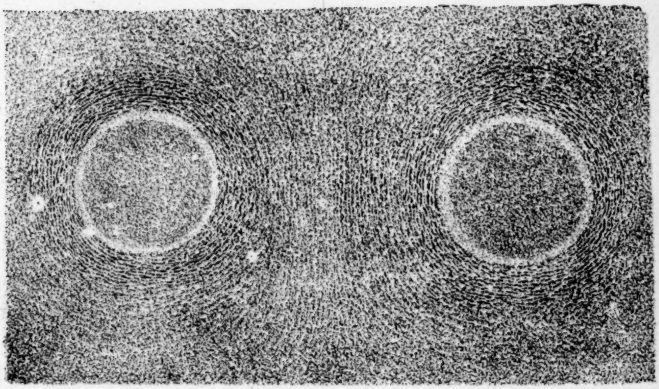

FIG. 1.

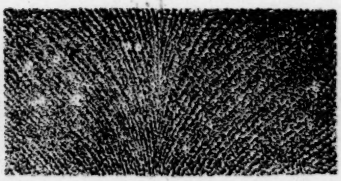

FIG. 2.

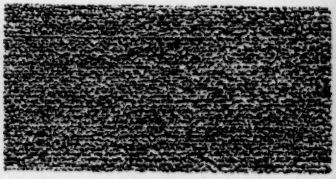

FIG. 3.

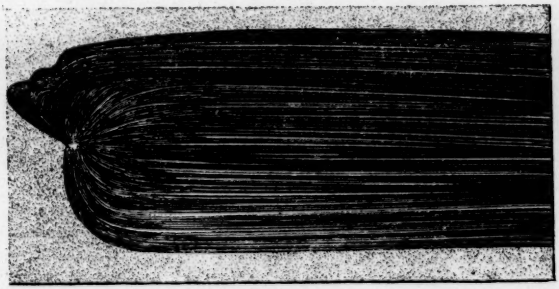

FIG. 4.

7th. That the deposition in ridges when copper is deposited on iron in a magnetic field may be due to similar action.

As will be seen, most of the effects described which have been attributed to the influence of magnetism on chemical action are due to secondary causes.

The "protective" effect first observed by Prof. Rowland is *now* the only incontestable evidence in favor of any direct effect.

As was stated above, this is very small indeed and probably finds its explanation in the increased work necessary to bring into solution the iron against the forces of attractions of the body of the metal when this is magnetized.

Postscript.[1]

After the publication of the article in which the experiment which formed the starting point of this investigation was described, Prof. Remsen endeavored to find similar effects by replacing iron plates by plates of other metals and the copper sulphate solution by solutions of other metallic salts which are precipitated by the metal of the plates. Thus it was found that the action of copper and silver solutions on zinc and aluminium was apparently uninfluenced by placing the plates between the poles of an electro-magnet. This was also found to be the case in the action of copper solutions on tin and silver solutions on lead. In no case was the deposited metal arranged in well-defined ridges. These were also absent in the action of bismuth, silver, and mercury solutions on iron, platinum, and gold solutions (in *aqua regia*) on nickel. In all the experiments with iron and nickel, the outlines of the poles were well defined by a region of no deposit.

Prof. Remsen next experimented on the action of acids on metal strips placed in glass troughs on the upright poles of a horse-shoe magnet. Using iron and nickel strips and nitric acid, it was found that those parts of the strips directly over the poles were protected, though similar experiments with copper, zinc, and magnesium strips showed exactly the same effect.

The action of dilute hydrochloric and sulphuric acids on iron seemed to be fairly uniform but in these experiments the action was very slow.

[1] Since the publication of my first article on "Chemical Action in a Magnetic Field" (*loc. cit.*) I have done a good deal of work on the subject, but, in the main, the results have been disappointing. I have now placed my laboratory note-books at the disposal of Dr. Wolff with the request that he would make such use of them as seemed best, my direct interest in the matter having long since ceased. I. R.

The results obtained with the non-magnetic metals suggest that this phenomenon may, in part at least, be due to the cooling influences of the iron poles, and, moreover, this influence would be less marked the slower the action.

The interpretation of these experiments was still further complicated by the presence of the rotations observed in the liquid. These rotations are oppositely directed over the two poles.

A large number of *quantitative* experiments were also made on the action of acids on metal wires contained in test-tubes which were placed in the hollow core of a coil of wire through which an electric current was flowing, parallel experiments being always made in which the reaction took place in an exactly similar coil through which no current was flowing. Although it was found that copper wires were dissolved more rapidly within the coil carrying the current (due most probably to the increase of temperature arising from the heat generated by the current) iron wires were *less* rapidly dissolved, showing undoubtedly that the iron wires were protected in the magnetic field. It seems, however, that the protection observed is due not to the *direct* influence of magnetism, but to the accumulation of the iron salts formed in the reaction about the strongly magnetized ends of the wires. Accordingly, the protection should be less when the iron dissolves as ferrous salt than when it dissolves as ferric salt.

The results obtained with hydrochloric acid and with sulphuric acid were, therefore, not always uniform, as the protection was counteracted by the heating of the coil. This was also found to be true with nickel and nitric acid.

In a third set of experiments, the reaction was carried on in test-tubes between the poles of a large electro-magnet. The same general results were obtained as before, exceptions being readily accounted for by the variations in temperature, which would be produced by the proximity of the large iron pole-pieces and the heat generated in the coils of the electro-magnet, and subsequently conducted to the pole-pieces.

Hunt's Experiments.

Prof. Remsen then repeated the experiments of Robert Hunt.[1] but was unable to obtain any of the curious effects

[1] Mem. Geol. Sur. of Gt. Brit., 1, 433; Phil. Mag. (3rd series), **28**, 4; and *Ibid*, (3rd series), **32**, 252.

claimed to have been obtained. Some of these are described below.

1. *Deposition of Silver on Copper in a Magnetic Field.*—On pouring a weak solution of silver nitrate over a copper plate surrounded by an edging of wax and placed on the poles of a magnet, the precipitated silver, according to Hunt, arranges itself in curves radiating spirally in opposite directions from two points directly over the poles, and, if the reaction be allowed to continue, it will be found that "the acid of the silver salt has bitten deeply into the plate" in parts bearing definite relations to the position of the poles.

No effect of this kind could be obtained.

2. *Reduction of Silver Nitrate by Ferrous Sulphate.*—If solutions of these salts are mixed in a vessel placed on the poles of a magnet, according to Hunt, the reduced silver arranges itself in definite curves. Attempts made to verify this statement were also unsuccessful.

3. *Action of Mercury on Silver Solution in a Magnetic Field.*—The statement, that globules of mercury precipitate the silver in curves depending on the position of the poles, could not be verified.

4. *Action of Ferrous Sulphate on Silver Solution.*—Small tubes filled with a saturated solution of ferrous sulphate were inverted directly over the poles of a magnet, on which was placed a vessel containing a solution of silver nitrate. The precipitated silver was *not* arranged in "diamagnetic curves" (so called because they seemed to repel each other as they approached) as claimed by Hunt.

5. *Crystallization in a Magnetic Field.*—Experiments were made with solutions of ferrous sulphate and potassium ferrocyanide, but no influence of the field on the crystallization could be detected.

6. *Reduction of Ferric Sulphate in a Magnetic Field.*—Prof. Remsen next determined the rate at which an acidified solution of ferric sulphate is reduced by iron wires, both within and without a magnetic field. The differences observed were both positive and negative and did not exceed the experimental error.

Since then, Loeb[1] has studied both the rate of reduction

[1] This Journal, **13**, 145.

and that of oxidation of iron salts by reducing and oxidizing *solutions* in a magnetic field, but he too reached the same conclusion as that arrived at by Prof. Remsen.

The experiments by Wartman[1] on electrolysis in a magnetic field were also repeated, copper being electrolyzed from a solution of the sulphate, and iron from a solution of ferric sulphate in potassium and ammonium oxalate. The results obtained were negative as were those of Wartman.

During the winter term (1893) the experiments of Robert Hunt[2] were again repeated by the writer. A few of the effects described could be reproduced, but these, it was found, could just as well be obtained without the aid of magnetism. In the first of Hunt's experiments described above, no such effect could be obtained, but even if it had been, this would have furnished no evidence of the influence of magnetism on chemical action, since there can be no possible connection between spiral ridges and the magnetic field which exists about the poles of a horse-shoe magnet. However, on pouring a weak solution of silver nitrate over a circular disk of copper fitted to the bottom of a crystallizing dish, it was noticed that the silver *was* deposited in spirals if the solution was poured in tangentially so as to give it a rotary motion. By the movement of detached silver particles it was made evident that the spirals marked the *lines of flow* of the liquid in contact with the plate, and consequently, when the solution was poured in from the opposite direction, the direction of the spirals, which become obliterated as the thickness of the silver deposit increases, is also reversed. It is possible that Hunt may have observed some such phenomenon, but it is difficult to see how it could have been produced in the rectangular vessels he used. No "bitten spaces" were ever observed, although silver solutions of various concentrations were used. In the experiment in which silver was precipitated from a solution of silver nitrate by a solution of ferrous sulphate, the spirals, in which the metal was deposited, were probably lines of flow of the solution, as the same effects can also be obtained without the aid of magnetism. In the modification of the foregoing experiment, in which a solution of

[1] Phil. Mag. (3rd series), **36**, 30. [2] *Loc. cit.*

ferrous sulphate was allowed to diffuse from inverted tubes into a solution of silver nitrate, the "diamagnetic curves" observed are merely lines of flow of the diffusing iron solution, as is readily shown by repeating the experiment without the aid of a magnet.

One of the experiments made by Prof. Remsen in connection with his repetition of Hunt's work, consisted in placing a crystal of mercuric chloride on a copper plate covered with water. It was found that the mercury was deposited on the the copper in "diamagnetic curves" (as Hunt would have called them) radiating out from the dissolving crystal, and, moreover, it was found that the same result was obtained both within and outside of a magnetic field. By *tilting the plate* it can easily be shown that the curves merely mark the lines of flow of the mercury solution formed by the dissolving crystal, for now the curves proceed in the direction in which the solution would flow if subjected only to the action of gravity.

The reason why a metal is precipitated in ridges along the lines of flow of a solution of one of its salts flowing over a plate of a second metal capable of precipitating it, has yet to be given. That the explanation is entirely mechanical is quite improbable, for the ridges are formed even when the velocity of the flow is comparatively small. In the course of the investigation the following explanation has suggested itself:

Consider, for example, the ridges formed by a solution of copper sulphate flowing over a tin plate. The action first begins at the source of flow and, wherever any copper is deposited, a solution of tin is formed. This is carried along by the motion of the copper sulphate solution, and, as the tin *must* go into solution at the surface of the plate, the liquid, directly in contact with the plate, becomes streaked with alternate streamers of copper solution, and tin solution. An electromotive force of considerable magnitude is thus established between adjacent portions of the surface, and necessarily gives rise to a large amount of electrolysis on account of the very low resistance of the local voltaic circuit established. More tin goes into solution in the streaks where it already exists; these become more pronounced, and thus assure the permanence of the ridges.

As was stated above, when an iron plate is placed in an

inclined position in a solution of copper sulphate, the copper sulphate on its *under* surface is found to be deposited in ridges. Streams of yellow iron solution, corresponding to the ridges, are observed to rise vertically from the rim of the plate in the clear blue copper solution above. In this case the solution in immediate contact with the under surface of the plate consists of alternate streamers of iron and copper solution, and the ridges are always in the direction in which gravity would cause the lighter iron solution to flow. Consequently the upper surface is only streaked when the plate is nearly vertical.

U. Behn[1] has lately shown that the ridges often observed in the Poggendorf silver-voltameter are produced by a flow resulting from the increased concentration of the silver solution about the anode (due to the unequal velocities of the ions). The cases examined by him were those in which the solution of a metal was *electrolyzed* between electrodes of the same metal, and the explanation of the phenomenon seems to be that the flow of the concentrated solution from the anode gives rise to a streaky condition of the solution, thus correspondingly changing its conductivity; and, therefore, the current-density on different parts of the cathode. Here too, as would be expected, the ridges mark the lines of flow of the concentrated silver solution over the surface of the cathode, and are, therefore, only observed when the cathode is directly beneath the anode.

The part which *magnetism* plays in the formation of ridges when a solution of copper sulphate is poured over an iron plate seems then to consist principally in giving rise to an unequal distribution of the iron salts formed in the reaction, to which most of the effects are *directly* attributable; in the production of electro-magnetic rotations in the solution; and in preventing the lighter iron solution from rising to the surface, thus assuring the permanence of electromotive differences once established.

[1] Wiedemann's Annalen, **51**, 105. Ueber die streifenförmige Anordnung Galvanischer Niederschläge.

PHYSICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
March, 1894

REVIEWS.

A TEXT-BOOK OF INORGANIC CHEMISTRY. G. S. NEWTH, F. S. C., F. C. S., Demonstrator in the Royal College of Science, London; Assistant Examiner in Chemistry, Science, and Art Department. London: Longmans, Green & Co., 1894. 667 pp.

In the preface Mr. Newth says: "In drawing up a systematic course of elementary chemical instruction based upon the periodic classification of the elements, a number of serious difficulties are encountered. I have endeavored to obviate many of these difficulties while still making the periodic system the foundation on which this little book is based by dividing the book into three parts. Part I contains a brief sketch of the fundamental principles and theories upon which the science of chemistry is built. Part II consists of the study of the four typical elements, hydrogen, oxygen, nitrogen, and carbon, and of their more important compounds. In Part III, the elements are treated systematically, according to the periodic classification."

Glancing at the table of contents, one finds that Part I contains fifteen chapters, covering 142 pages. These chapters contain all of the theoretical considerations which are scattered through the pages of most chemical text-books, and under the heads of general properties of liquids, electrolysis, solutions, osmotic pressure, thermo-chemistry, much that is usually omitted in elementary books.

The involuntary feeling of surprise at such a beginning, is tempered by noting a page entitled "Hints to Students," which follows the preface. The student is advised first carefully to read the first four chapters, pages 1 to 23, then to pass on to Part II, and to study the four typical elements and their compounds. During the time occupied in the study of these four elements, the student should "fairly master at least the first thirteen chapters of Part I." The first four chapters of Part I treat of chemical change, molecules, atoms, elements and compounds, chemical action, nomenclature, and other matters commonly taken up in the earlier chapters of text-books. On carefully examining these four chapters, however, the feeling of surprise returns. Whether definitions of mono and diatomic molecules, acidic and basic oxides, catalytic action, peracids, hypoacids, oxyacids, and thioacids, basicity of acids, can convey any meaning to the mind of a student who is not supposed to know anything of hydrogen or oxygen, is questionable.

Part 2 contains 150 pages. The present writer commends, to advanced students, a careful study of these chapters; closely condensed, thoughtful and suggestive they include a mass of

information found in few advanced text-books. One example may suffice. Among nitrogen compounds, hydrazine, hydrazine hydrate, hydrazoic acid, hydroxlamine, the ammonsulphonates and their hydroxylamine derivatives, the halogen compounds of nitrogen are briefly but lucidly discussed. Under the head of nitrogen iodide, the work of Courtois, Gladstone, and Lzuhay is clearly explained, though that of Mallet is not mentioned.

But this book is an elementary text-book, and the student has not yet taken up the study of the halogens. For him Part II seems at once too condensed and too full.

The "mastery" of the first thirteen chapters of Part I should now follow. Valency, atomicity, electrolysis, the constitution of hydrofluorsilicic acid and its analogues seem difficult to master before studying the properties of hydrochloric acid, or of any metals or bases.

The book is based on the periodic system. In the explanation of the system in the chapter devoted to it in Part I, and throughout part III, the author omits deductions from the system that would have been helpful to the student. For example, on page 338, the constitution of the oxyacids of chlorine is discussed. The structure of chloric acid Cl—O—O—O—H is given, and the author continues: "It is possible that in some of these compounds the chlorine functions as a trivalent element, and that these compounds have a constitution similar to the oxides and oxyacids of nitrogen, thus, chloric acid, $H—O—Cl\begin{smallmatrix}/\\ |\\ \backslash\end{smallmatrix}\begin{smallmatrix}O\\ |\\ O\end{smallmatrix}$; nitric acid $H—O—N\begin{smallmatrix}/\\ |\\ \backslash\end{smallmatrix}\begin{smallmatrix}O\\ |\\ O\end{smallmatrix}$." Later he says: "Indeed, from a consideration of the salts of periodic acid, some chemists are in favor of assigning to iodine even a greater valency, and of regarding it as a heptad element in these compounds." In discussing the periodates, he speaks clearly of the many hypothetical periodic acids from which the salts known may be regarded as derived, but nowhere does he show how all of the oxyacids of the halogens may be simply classified and explained by the hypothesis of a halogen valence varying from 1 to 7, as suggested by the position of the halogens in the periodic system.

Again, the structure above given for nitric acid is the only one the present writer has found in the book. The author derives the phosphoric acids from pentavalent phosphorus, giving structural formulas, and says that the acids of arsenic and antimony correspond to those of phosphorus. Surely most chemists regard nitric acid as corresponding in structure with metaphosphoric acid, and think that the pentavalence of nitrogen in nitric acid follows from its position in the periodic system.

It would be captious to seek too closely for faults in a book which has much to recommend it, and while the present writer cannot think either the arrangement of the book, or its mass of condensed information suitable for an elementary text-book, these very qualities make it valuable as a handy reference book for the advanced student. Its thoroughness, its lucidity, the admirable way in which, for example, a subject so hackneyed as the methods of preparing oxygen, is made new and full of interest cannot be too highly praised. The many teachers who feel grateful to Mr. Newth for his admirable "Chemical Lecture Experiments" would look for these qualities in any book written by him, and will not lay this book aside without gratitude for many fresh suggestions on the most familiar subjects. E. R.

NOTE.

The Relative Behavior of Chemically Prepared and of Atmospheric Nitrogen in the Liquid State.

The following abstract of a communication[1] by Professor James Dewar to the December meeting of the Chemical Society of London is of interest in connection with the subject of the discovery announced last summer by Lord Rayleigh and Professor Ramsay of a supposed new element in the air:

When gases, such as nitrogen, oxygen, or air, are liquefied in large quantities, the impurities found in the gases and taken up during the passage through the pumps gradually accumulate, and when the fluids are discharged into vacuum vessels at atmospheric pressure these separate in the solid state. If the solid matter is filtered off from liquid air and the fluid allowed to evaporate slowly from a vacuum vessel, then the last drops of liquid are almost pure oxygen; nitrogen gas containing 3 or 4 per cent. of oxygen when liquefied behaves exactly in the same way. It would appear, therefore, that no impurity of higher boiling-point than oxygen can be separated by ordinary fractional distillation of the liquid air, and if any other material is present it must evaporate along with the nitrogen. By the use of a special arrangement, small quantities of gases, in a pure and dry state, amounting to from 100 cc. to a few liters, may be examined in the liquid condition and the experiment repeated as often as desired with the same specimen of gas.

The simple apparatus exhibited, by means of which the condensing-point of a gas and afterwards the volatilizing rate

[1] Before reading his paper, Professor Dewar exhibited a vacuum-jacketted globe containing about half a liter of liquid air, which had been kept for the previous thirty hours at the Royal Institution.

of the resulting liquid may be observed, may be succinctly described as follows:—A tube of small bore, somewhat drawn out at one extremity, is passed nearly to the bottom of a distillation flask and sealed into the neck. The outer portion of this tube is closed and bent twice at right angles, so that a closed limb is thus formed outside the vessel. The side tube of the flask is sealed after the pure, dry gas under examination has been introduced, together with phosphorus pentoxide, at a known pressure and temperature. The closed limb of the small bore tube is then cautiously introduced into a vacuum-jacketted tube containing liquid air or oxygen, so arranged that the vapor pressure on the liquid may be gradually lowered by means of an air pump, and the gas within the tube slowly reduced to the temperature of liquefaction. In this way it is easy to observe the point at which liquid begins to form from different samples of gas placed side by side, and afterwards, when the temperature of the liquid air-bath is allowed to rise, the point at which the last drops of the liquids resume the gaseous form. Nitrogen obtained from atmospheric air has been compared in this manner with nitrogen prepared from nitric oxide without any differences between them being detected. Atmospheric nitrogen which has been passed over heated magnesium showed, however, a marked difference as compared with gas which had not been so treated. Although its condensing-point was not far removed from that of the untreated material, as a matter of fact this point, as well as the volatilizing-point of the resulting liquid, was higher than before, that is to say, nitrogen which has been passed over heated magnesium becomes liquid a little before the original specimen, and the liquid evaporates rather more slowly and lasts longer when both substances are compared under precisely similar circumstances. Nitrogen, chemically prepared from nitric oxide, was likewise changed by passing it over heated magnesium, for after this operation it liquefied and evaporated at a rather higher temperature than previously.

It would, therefore, appear that, whilst atmospheric nitrogen does experience change when passed over heated magnesium, some effect is also produced on chemically prepared nitrogen; and, as far as these experiments have been carried, they reveal no very marked difference between the behavior of nitrogen from atmospheric air and nitrogen obtained from its compounds by chemical methods. It may be, however, that any concentrated impurity boils nearly at the same temperature as the original nitrogen, or that the amount present is so small that it does not liquefy at the temperature of —200° C. Considering that the flasks of 150 cc. capacity contained

the concentrated impurity of 10 liters of nitrogen, the partial pressure of small quantities of other matter ought to be very considerable, so that we might anticipate liquefaction at —200° C. At the lowest temperature reached, atmospheric nitrogen which had been passed once over magnesium gave clear, transparent crystals along with liquid, while the untreated nitrogen remained fluid. All the samples of nitrogen and oxygen properly purified, when liquefied in the above manner, are clear, transparent liquids, so that the solid matter which always separates when air or nitrogen or oxygen is liquefied on the large scale consists of impurities. If a manometer is attached to the flask containing the gas, and at the same time the condensing-tube is calibrated, the method of working gives quantitative results, since the pressure in the flask and the volume of liquid condensed can be simultaneously observed.

Further, if we use liquid oxygen as the cooling agent, we can observe the vapor pressures of two or more substances at the same temperature, and these pressures may be expressed in terms of the vapor pressure of oxygen. In this way all very volatile liquids would be comparable with oxygen as a standard.

It must be understood that these experiments are merely qualitative, and were not carried out with the view of separating any new substance from air or nitrogen. Their chief object is to observe the points of condensation and evaporation of gases liquefying between —180° C. and —200° C. at and below atmospheric pressure.

Small amounts of known impurities cause marked differences in the amount of liquid formed from the same volume of gas similarly treated. Thus, a trace of impurity, presumably hydrogen, in a sample of nitrogen subjected to liquefaction in the above manner only gave one-third the volume of liquid that a similar flask gave when filled with pure nitrogen. This is due to the concentration of the hydrogen or other non-liquefiable material in the narrow tube where liquefaction takes place.

This plan of working may be conveniently applied to testing whether the oxygen and nitrogen in air liquefy simultaneously. Such a question cannot be answered by liquefying air under pressure. If, however, two flasks, such as have been described, are taken, one filled with nitrogen at 0.79 of the atmospheric pressure, and the other with oxygen at 0.21 of the atmospheric pressure (the temperatures being equal), then, on cooling them side by side, the instant at which liquefaction takes place in the narrow condensing tubes can be observed. The oxygen always appears a few seconds before

the nitrogen, and remains after the latter has evaporated. The boiling-points of nitrogen and oxygen, under the respective pressures at which they exist in the atmosphere, are very close together.

In the discussion which followed this communication, the President, referring to experiments on the liquefaction of gases which he had recently witnessed in the Royal Institution Laboratory, said that the means of producing very low temperatures during long periods, now at Professor Dewar's disposal there, were marvellously complete, and important results ought, before long, to flow from their application.

It was useless to deny that special interest attached to the communication to which they had just listened, but, unfortunately, in the absence of Lord Rayleigh and Professor Ramsay, they were left in the position of having to play "Hamlet" with only the ghost present, and, under such circumstances, the play obviously could not be continued to a successful issue. Chemists were deeply interested by the statements relating to the discovery of a new constituent of the atmosphere, brought before the British Association at Oxford, but they awaited further information before making up their minds. They were in a very different position, however, since Friday last, when the President of the Royal Society, in his address, referred to this discovery as the greatest scientific event of the year. It was to be supposed that the President of the Royal Society had information at his disposal, not hitherto made public, which justified so definite a statement, and naturally chemists would impatiently await its disclosure. He ventured to say that Lord Rayleigh and Professor Ramsay now could not hope to keep so remarkable a discovery to themselves much longer. After having been told so much, chemists could not be expected to remain quiet under the imputation that they had been eyeless during a whole century, and they would undoubtedly inquire into the matter. Although no one would seek to take the discovery out of the hands of those who had announced it, chemists unquestionably had the right, not only to exercise entire freedom of judgment, but also to critically examine the statements which had been made. With regard to Professor Dewar's observations, which were such as could only be made with the aid of the low temperature appliances at his disposal at the Royal Institution, Professor Dewar would be the first to admit that they were of a qualitative character, and open to several interpretations; but they were certainly highly suggestive.